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# TABLE OF CONTENTS

1964-65

## SUMMER SESSION - 1964

|  | Page |
|--|------|
| A STUDY OF ISOPOLYANIONS IN AQUEOUS SOLUTION -<br>Wilfred H. Nelson  | 1    |
| COORDINATION CHEMISTRY OF SELENIUM -<br>Monther Y. Aljanahi  | 8    |
| STRUCTURE OF METAL ALKOXIDES - Mark Wicholas   | 15   |
| THE ELECTRONIC STRUCTURES OF COPPER(II) ACETATE<br>and RELATED COMPOUNDS - Michael F. Rettig                   | 21   |
| THE USE OF HIGH-SURFACE-AREA-SILICA GELS FOR<br>OBSERVING AND MEASURING ION-SOLVATION -<br>Kenneth C. Williams | 33   |
| HYDRIDO COMPLEXES OF TRANSITION METALS -<br>Mahdi N. Al-Zagoum   | 39   |

## FALL AND SPRING SESSION - 1964-65

|   | Page |
|---|------|
| SOME ORGANOMETALLIC CHEMISTRY OF GROUP IIB -<br>Larry M. Seitz  | 50   |
| RECENT CORRELATIONS BETWEEN STRUCTURAL VARIATIONS<br>IN A SERIES OF MOLECULES AND THEIR CHEMICAL<br>PROPERTIES - Donald Dugre | 59   |
| SOME TRAPPED RADICAL STUDIES - Michael Garrett  | 67   |
| MICROPOTENTIOMETRIC STUDY OF CHLORIDE BINDING<br>TO MOYOGLOBIN - Hassan Tayim   | 72   |
| ALKYNE-BRIDGED TRANSITION METAL COMPLEXES -<br>R. E. Wagner   | 77   |
| THE TRANSITION-METAL CARBONYL HYDRIDES AND<br>DERIVATIVES - Anton Schreiner   | 85   |
| RECENT CHEMISTRY OF PHOSPHOROCHLORIDES -<br>V. Alan Mode  | 107  |
| SOME APPLICATIONS OF GAS CHROMATOGRAPHY TO THE<br>SEPARATION AND IDENTIFICATION OF METAL COMPOUNDS -<br>James Murphy          | 108  |



## A STUDY OF ISOPOLYANIONS IN AQUEOUS SOLUTION

Wilfred H. Nelson

June 16, 1964

### I BACKGROUND

Recently there has been some interest in the isopolyanions formed in aqueous solutions of the transition metals, primarily with Group V-B and VI-B elements. Studies on solutions of vanadium (V) by e.m.f. techniques have indicated a decavanadate  $[V_{10}O_{28}]^{-5}$  and  $[H_2V_{10}O_{28}]^{-4}$  in the pH range 4 to 6. Studies by other experimental methods including measurement of the visible absorption spectrum,<sup>1</sup> ultracentrifugation,<sup>2</sup> and cryoscopic studies<sup>3,4</sup> have tended to confirm these results. E.m.f. studies have also indicated that the smaller poly- and mono-nuclear anions,  $[V_3O_9]^{-3}$ ,  $[HV_2O_7]^{-2}$ , and  $[HVO_4]^{-2}$ , also exist in solutions in the pH range 8 to 10.<sup>5</sup>

Few solution studies have been carried out with the heavier V-B elements because their extremely basic nature makes such experiments difficult. Jander and Ertel<sup>6</sup> recently studied solutions containing niobium (V) using conductometric, u.v. spectrophotometric, and diffusion techniques. They reported that strongly alkaline solutions contained an anion  $[Nb_6O_{19}]^{-8}$  and that this could be protonated to give  $[HNb_6O_{19}]^{-7}$ . On the other hand similar studies made on solutions of tantalum (V) led to the postulation of a pentatantalate.<sup>7</sup> These conclusions were drawn largely from measurements of diffusion coefficients and cryoscopic studies. Both of these experimental methods have been criticized.<sup>8,9</sup>

The polyanions of the Group V-B elements have been the subject of many investigations. Recently Schwarzenbach and Meier<sup>10</sup> found that both  $HCrO_4^-$  and  $[Cr_2O_7]^{-2}$  exist in acidified solutions of Cr(VI). Recent studies of Mo(VI) solutions using e.m.f. methods indicate that the polyanion  $[Mo_7O_{24}]^{-6}$  plus the protonated species  $[HMo_7O_{24}]^{-5}$  and  $[H_2Mo_7O_{24}]^{-4}$  exist in the pH range 5 to 6.<sup>11</sup> An early light scattering work<sup>12</sup> indicated large polyions existed in acidified molybdate solution, and a recent light scattering study<sup>13</sup> indicated that the ion contains seven molybdenum atoms. Very recently it was shown by equilibrium ultracentrifugation<sup>14</sup> and by raman spectroscopy that ions containing either seven or eight molybdenum atoms exist in acid aqueous solution. X-ray studies<sup>15</sup> show that these same species,  $[Mo_7O_{24}]^{-6}$  and  $[Mo_8O_{27}]^{-6}$  are present in the solid state.

Both e.m.f.<sup>16</sup> and ion exchange<sup>17</sup> studies indicate that anions containing six tungsten atoms and with net charges of minus 2 exist in acid aqueous solution. These are written most simply as protonated forms of  $[HW_6O_{21}]^{-5}$ .

Since the stereochemistry of tantalum in oxygen compounds is rather simple, it was decided to study alkaline tantalate solutions as a model system for the investigation of polyanion formation. The potassium tantalate,  $K_8Ta_6O_{19} \cdot 16H_2O$ , is extremely soluble in water and appeared suitable for study. X-ray work<sup>18</sup> on the crystals has shown that they contain hexatantalate anions of cubic symmetry.

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## II THE PROPOSED METHOD OF ATTACK

The essentially independent methods of e.m.f. measurements, light scattering, and equilibrium ultracentrifugation provide the necessary basic information to determine the charge and degree of polymerization of anions existing in alkaline aqueous solution. E.m.f. studies using a glass electrode make clear the concentration ranges where the polymerization reactions are rapid and reversible. Under favorable conditions the formulas of the polymers predominating in each region can be determined and stability constants calculated. Charge transfer bands in the ultraviolet should indicate the presence of any new species by a shift in the absorption region.

Finding regions where one isopolyion predominates is possible. Such monodisperse systems can be subjected to analysis by light scattering. Tobias and Tyree<sup>19</sup> have outlined the theory for such work and have successfully applied it to the hydrolyzed bismuth (III) system.<sup>20</sup>

With sufficiently stable solutions, equilibrium ultracentrifugation using methods developed by workers at Oak Ridge<sup>21</sup> should give a good check on the reliability of the light scattering results. Use of both schlieren<sup>22</sup> and interference-type<sup>23</sup> optics should provide an additional experimental check over a wide range of polyion concentrations.

Finally, it would seem reasonable to bind tantalates to an anion exchange resin,<sup>24</sup> and after measuring the equilibrium pH to determine maximum charge from the hydroxide ions displaced. Also if several species existed it might be possible to separate them by eluting with KOH solutions.

As a check on the precision and accuracy of light-scattering and ultra-centrifugation measurements, it was planned to use well-characterized potassium 12-tungstosilicate solutions as a model for a detailed study. The use of these solutions as "knowns" is justified since x-ray diffraction studies<sup>25</sup> on 0.3095 M  $H_4SiW_{12}O_{40}$  solutions have confirmed that the single polyanion existing in these solutions is the same as that found in the crystals, i.e.,  $[SiW_{12}O_{40}]^{-4}$ . Complementary light scattering<sup>26</sup> and ultracentrifuge<sup>27</sup> work has also been done.

## III OUTLINE OF EXPERIMENTAL TECHNIQUES

### E.m.f. Measurements

Methods for studying complex equilibria have been developed in great detail for systems involving both mononuclear<sup>28,29</sup> and polynuclear<sup>30,31</sup> species. Data are usually gathered and expressed in terms of an average ligand number  $\bar{n}$  or  $z$ , equalling the average number of ligands bound per metal atom. For an unknown system containing the various species  $M_nX_m$ , where B is the total concentration of metal, M; A is the total (analytical) ligand concentration, b is the equilibrium concentration of the free ligand,  $X^-$ ; and  $K_{pq}$  is the equilibrium constant for formation of the species: given A,  $K_{pq}$  and B to good precision all  $K_{pq}$ 's



can be calculated. If only mononuclear species  $MX_p$  are present in solution, the ligand number  $n$  will be independent of  $B$ . Thus, if for such a system "a" represented the hydroxide ion concentration a plot of the ligand number vs. pH would be independent of  $B$ .

Such plots contribute information which can be used to find regions of monodispersity if such exist. This latter condition is most important in light scattering and equilibrium ultracentrifugation. Polydisperse systems at present seem too complex to be subject to successful analysis.

### Light Scattering

Einstein<sup>32</sup> first suitably explained the turbidity of liquids as due to local thermal fluctuations in density. Solutions are more turbid than pure liquids since local differences in concentration augment solvent thermal irregularities in the refractive index. Debye<sup>33,34</sup> reduced the turbidity equation to one containing easily measured quantities. Stockmayer<sup>35</sup> and independently Kirkwood and Goldberg,<sup>36</sup> developed a general equation for the fluctuations of the refractive index in multicomponent systems with no angular dissymmetry permitting the interpretation for such systems.

Tobias and Tyree<sup>19</sup> have developed the following modification of the equation of Stockmayer for solutions of low molecular weight polymeric electrolytes in the presence of high concentrations of supporting electrolytes.

$$\frac{1}{N_{Z'}} = \frac{H^0 \psi'^2 m'}{\gamma^*} - \frac{Z'^2 m'}{2m_3} \quad (1)$$

The equation is written for a monomeric component defined to be  $K(1.34 - \gamma) K_2 TaO_{3.16} - \frac{(1.34 - \gamma)}{2} KCl$ . Thus,  $N_{Z'}$  represents the degree of polymerization;  $\psi'^2$  is the molar refractive index increment of the component;  $m'$  is the component molarity;  $\gamma^*$  is total solution turbidity minus supporting electrolyte turbidity.  $Z' = 1.34 - \gamma$  where  $\gamma$  is the number of potassium ions bound per monomer component.  $\phi$  is the volume fraction of the solvent; and  $m_3$  is the concentration of the supporting electrolyte.

Essentially, equation 1 has two unknown quantities,  $N_{Z'}$  and  $Z'$ . Theoretically, measurements of turbidities of two solutions of different  $m'$  should suffice to solve for  $N_{Z'}$  and  $Z'$ . In practice it is best to measure several solution turbidities over as wide a range of  $m'$  concentration as possible. Plotting  $1/N_{Z'}$  as a function of  $Z'$  for each concentration of polymer in solution is perhaps a more accurate method of determining the experimental quantities. A family of smooth curves results which intersect at the best values of  $1/N_{Z'}$  and  $Z'$ .

### Ultracentrifugation

The general theory of sedimentation equilibrium has been outlined by Svedberg and Pedersen.<sup>37</sup> For a solution containing a sedimenting component  $i$ ,







$$\ln a_i = \frac{M_i(1-v_iPx)w^2d(x^2)}{2RT} \quad (2)$$

$a_i$  = activity of component  $i$ ,  $M_i$  = molecular weight,  $v_i$  = partial specific volume,  $P$  = density of solution, and  $w$  = angular velocity of the rotor. If the activity coefficient is constant a plot of  $\ln m'$  vs.  $x^2$  will allow one to calculate  $M_i$  for a nonelectrolyte. However, if the solute is ionized one must know the charge,  $Z'$ , to solve for  $M_i$ .

For charged species the sedimentation equation becomes

$$N_{Z'} = \frac{S/A'}{1 - \frac{(Z')^2 m' S}{2m_3 A'}} \quad (3) \quad \text{where} \quad A' = \frac{M'(1-v_iPx)w^2}{2RT} \quad (4)$$

Actually with schlieren optics what is measured is  $S_e = d \ln(Z^*/x/d(x^2))$  where  $Z^*$ , the displacement of the bar image, is proportional to the refractive index gradient at  $x$ . The relationship between  $S_e$  and  $S$  is as follows.  $S_e - S = d \ln S / d(x^2)$ . Calculation of  $N_{Z'}$  and  $Z'$  therefore requires measuring  $S_e$  for solutions of varying solute concentration, calculating  $A'$  and  $S$ , and solving for  $N$  for assumed values of  $Z'$  for each of these solutions. The intersection of  $N_{Z'}$  and  $Z'$  plots for the various solutions will indicate the best value for  $N_{Z'}$ , just as is done for the light scattering.

In the past five years interference optical systems have been described<sup>23,27,38</sup> which follow changes in concentration of solutes by measuring directly the difference in refractive index. A double compartment cell replaces the single compartment schlieren cell. One section holds the solvent, polymer, and supporting electrolyte, while the other contains an identical solution minus the polymeric solute. The paired cell compartments are sector shaped, the same size, and occupy positions during centrifugation identical to one another, but for rotation about the centrifuge axis. Monochromatic light passes by way of slits on the cell bottom through each compartment and produces interference fringes when recombined on the far side. From the positions of the fringes at equilibrium the distribution of the solute as a function of the distance from the center of rotation can be determined. Again  $N_{Z'}$  and  $Z'$  are determined simultaneously using the results of two or more experiments run at varied solute concentrations.

#### IV EXPERIMENTAL RESULTS

Potential measurements were made using a lithium glass electrode and a calomel electrode system in 0.5 M KCl. The work showed that about 0.12 hydroxide ions appeared in solution for each tantalum atom dissolved as the tantalate salt. This amount did not vary much with pH to the point where hydrous  $Ta_2O_5$  precipitated irreversibly around pH 11.

Aqueous potassium tantalate absorbed strongly in the u.v. below 2600 Å. At 2100 Å the extinction coefficient was  $2.6 \cdot 10^4$  and apparently the peak was below 2000 Å since none was detected. No shift



in the band was observed as the total tantalum concentration and hydroxide concentration were varied. In the infrared region bands appeared for tantalate at 965, 910, 822, and 710  $\text{cm}^{-1}$ .

Potassium tantalate was successfully bound to Dowex 2-X4 anionic resin in the hydroxide form. From KOH displaced it was determined that the maximum charge per monomer unit was about 1.12 compared to the maximum possible 1.34.

Turbidity data showed that tantalate in 1  $\text{M}$  KCl has a degree of polymerization of about six and an effective ionic charge of about -2. Depolarization measurements indicated a species of high symmetry. The tungstosilicate in 0.5  $\text{M}$  KCl showed a degree of polymerization slightly greater than 1 and a charge of -2.

Schlieren centrifugation results agreed well with those of the light scattering. The precision was about the same and the values of  $N_z$ , and  $Z'$  were identical within experimental error. Interference data showed more scatter, but again did not disagree with the other data.

#### V CONCLUSIONS

E.m.f. measurements, u.v. spectra, and anion exchange chromatography have indicated that the tantalate anions in aqueous solution are probably of approximately the same stoichiometry as their crystalline counterparts. It seems very unlikely in the light of the e.m.f. data that any tantalate monomer such as  $[\text{TaO}_4]^{-3}$  exists in the solutions studied, i.e., below pH 13, since  $\bar{n}$  values remained constant and quite small as the pH varied. Even better evidence that tantalate solutions contained only one anionic species came from the schlieren and interference ultracentrifugations.

It is certain that the effective charge,  $Z'$ , is lowered much more by the binding of potassium ions from the supporting electrolyte than by hydrolysis. What the precise magnitude of  $Z'$  really means is subject to some interpretation. Values of  $N_z$  did agree within an experimental error of less than ten percent for both techniques. This study has shown that tantalate polyanions are of high symmetry and probably contain six metal atoms. It is very likely that the species present in solution is nearly identical to that found in the solid state. The effective charge on the hexatantalate is most likely between -2 and -3.

Use of solutions of the well-characterized, highly symmetrical 12-tungstosilicate anion as a "known" has provided a check on the validity of the approximations made in the theoretical treatment of light scattering and ultracentrifugation equations.





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## COORDINATION CHEMISTRY OF SELENIUM

Monther Y. Aljanahi

July 7, 1964

### INTRODUCTION

The selenium atom can be regarded as a Lewis acid and as a Lewis base, because it is an electron acceptor in compounds such as  $H_2Se$ ,  $D_2Se(1)$ ,  $SeSn(2)$ ,  $SCSe(3)$ , etc., and it is an electron donor in compounds such as  $SeO_3(4)$ ,  $Se_2Cl_2$ ,  $Se_2Br_2(5)$ ,  $SeCl_4(6)$ ,  $SeS_2$ , etc.

This seminar will consider the coordination chemistry of those compounds in which selenium is the central atom as well as those compounds in which selenium, in an anion, is a ligand.

### COMPOUNDS IN WHICH SELENIUM IS THE CENTRAL ATOM

#### SeCl<sub>4</sub>

Selenium, a third row element, would not be expected to show appreciable double bond character in the  $SeCl_4$ . One can obtain some estimate of the double bond character by using the procedure outlined by Mays and Dailey(7). Using the published data(8) for Se-Cl bond length in  $SeCl_4$  and the single-bond and double-bond covalent radii for Se and Cl, Bray(6) found that  $SeCl_4$  has approximately 21% ionic character, 73% single bond character and 6% double bond character. He also calculated the value of  $1 - |U_p|$ , where  $U_p$ , the number of the unbalance p electrons on the halogen, is given by

$$|U_p| = \left| \frac{(eqQ)_{molecule}}{2} - (eqQ)_{atom} \right|$$

If the value of  $1 - |U_p|$ , which is equal to 0.33 - 0.37 for  $SeCl_4$ , is plotted as a function of the electronegativity difference, 0.7(9) or 0.6(10) for  $SeCl_4$  the point falls on the line joining the carbon, germanium, and tin tetrahalides but deviates toward the line which includes the silicon tetrahalides and which is different because of appreciable double-bond character in these compounds.

In this comparison of  $SeCl_4$  with Group IV tetrahalides, it must be remembered that selenium differs from the elements of Group IV by lacking two p-shell electrons. Furthermore, published x-ray data indicate that the tetrahedral structure model is probably only approximate in  $SeCl_4$  which has six resonances while carbon germanium, silicon, and titanium were found to have four to sixteen resonances.(12)(13)



Se(CN)<sub>2</sub> and Se(SeCN)<sub>2</sub>

An x-ray structure determination by Hazell(14) shows that selenium cyanide is an orthorombic crystal which has unit cell dimensions  $a = 8.71$ ,  $b = 6.98$  and  $c = 13.41$  Å. The V-shaped molecules lie in parallel planes, 3.35 Å apart, perpendicular to c axis. This layer structure accounts for ease of cleavage of the crystals. Bond lengths(15) (standard deviation 0.1 Å) are Se-C = 1.86 Å, C-N = 1.42 Å and the bond angles (standard deviation 6°) Se-C-N = 177°, C-Se-C = 119°. Aynstey, Greenwood, and Sprague(15) have reported the selenium cyanide stretching frequencies which are given in Table 1.

The selenium cyanide molecule has C<sub>2v</sub> symmetry with eight infrared active and nine Raman active normal modes of vibration while selenium selenocyanate has C<sub>s</sub> symmetry in the crystal lattice.(16) Seven of the fifteen modes were observed while the other modes could not be observed because of the low frequencies.

Table 1

Stretching Frequencies of Selenium Cyanide

| <u>Frequency</u><br><u><math>\nu</math> (cm<sup>-1</sup>)</u> | <u>Assignment</u> |                     |                          |
|---|-------------------|---------------------|--------------------------|
| 2183  |                   |                     |                          |
| 2175  | antisym.          | C $\equiv$ N        | stretch                  |
| 608   | antisym.          | C - Se              | stretch                  |
| 516   | sym.              | C - Se              | stretch                  |
| 436   | sym.              | Se - C <sub>2</sub> | bending                  |
| 346   |                   |                     |                          |
| 336   | sym. antisym.     | Se -C $\equiv$ N    | bending                  |
| 312   |                   |                     | out of plane deformation |
| 302   |                   |                     | ?                        |

SeO<sub>3</sub><sup>2-</sup>

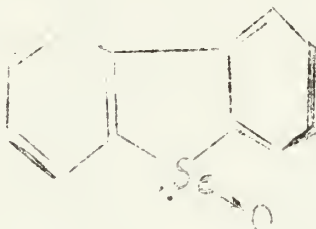
Riley(17) has prepared selenitopentamminecobalt (III) selenite [Co(NH<sub>3</sub>)<sub>5</sub>SeO<sub>3</sub>]<sub>2</sub>[SeO<sub>3</sub>].3H<sub>2</sub>O and [Co(NH<sub>3</sub>)<sub>5</sub>SeO<sub>3</sub>]Cl but his experiment did not show whether the selenite group is attached through selenium or oxygen.



## COMPOUNDS IN WHICH SELENIUM IS A DONOR ATOM

### Diarylseleno oxides

Gould and McCullough(18) have reported that diarylseleno oxides, such as dibenzoselenophene oxide (Figure 1)



(Figure 1)

coordinate to mercury (II) through the selenium atom in compounds  $(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{SeO} \cdot \text{HgCl}_2$ ,  $(p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{SeO} \cdot \text{HgCl}_2$ , and  $(\text{C}_6\text{H}_4)_2\text{SeO} \cdot \text{HgCl}_2$ , but no evidence was presented to support their conclusion.

### Selenocyanates (M-SeCN) and isoselenocyanates (M-NCSe)

The coordinating tendencies of the thiocyanate ion are well known, but relatively little is known about the selenocyanate ion. Selenocyanates have been found to be Se-bonded to metals of class (b) character(19), e.g.,  $\text{K}_2[\text{Pt}(\text{SeCN})_6]$ ,  $\text{K}_2[\text{Hg}(\text{SeCN})_4]$ , and  $\text{AgSeCN}$ , and N-bonded to metals of class (a) character such as  $\text{Co(II)}$ (20)(21) and  $\text{Cr(III)}$ , (22) e.g.,  $[\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCSe})_4]$  and  $\text{K}_3[\text{Co}(\text{NCSe})_6]$ . The third type of bonding of the selenocyanate ion, as a bridging group has been reported for  $\text{HgCo}(\text{NCSe})_4$ (20)(21)

It has been found, from x-ray structural determination, that the two mercury compounds  $\text{HgCo}(\text{NCSe})_4$  and  $\text{HgCo}(\text{NCS})_4$  are isomorphous.(20)(21)(23) Turco *et al.*, (21) have made the assumption that the nature of the coordination in selenocyanates must be similar to that of the corresponding thiocyanates.

The thiocyanate ion  $:\text{N} \equiv \text{C} - \text{S}^-$  is known to form both thiocyanato (M-SCN) and isothiocyanato (M-NCS) complexes depending on the central metal atom employed.(24) Recently, Pearson(25) has suggested that sulfur in the  $\text{SCN}^-$  ion is "soft" and tends to coordinate with a metal of class (b) (polarizable metal) character, whereas nitrogen in the  $\text{SCN}^-$  ion is "hard" and prefers to coordinate to a metal of class (a) (nonpolarizable metal) character.

Burmeister and Basolo(26) have reported the effects of a series of ligands on thiocyanate bonding in palladium (II) and platinum (II) complexes and the synthesis,(27) characterization and preliminary kinetics of the isomerization of thiocyanato and isothiocyanato isomers of some palladium (II) complexes. It is known that  $\text{NCS}^-$  does not depend on the metal





only to form N-bonded or S-bonded complexes but also depends on electronic and steric factors.(26)(28)

The C - N stretching frequencies of the selenocyanato complexes increase in the order  $M - NCSe < NCSe^- < M - SeCN < M - SeCN - M$ , which is different from the order observed for thiocyanates, namely,  $NCS^- < M - NCS < M - SCN < M - SCN - M$ .(29) The C - Se stretching frequencies shift, relatively to uncoordinated  $NCSe^-$ , to higher frequencies upon nitrogen coordination and to lower frequencies upon selenium coordination which is completely analogous to the behavior of the thiocyanates. Turco et al., (21) have reported that the C - N stretching frequencies of  $NCSe^-$  appeared to be less than  $2080\text{ cm}^{-1}$  for  $M - NCSe$  and greater than  $2080\text{ cm}^{-1}$  for  $M - SeCN$  while the C - Se stretching frequencies were around  $650\text{ cm}^{-1}$  ( $700\text{-}600\text{ cm}^{-1}$ ) for  $M - NCSe$  and around  $550\text{ cm}^{-1}$  ( $500\text{-}600\text{ cm}^{-1}$ ) for  $M - SeCN$ . Stretching frequencies of C - N, C - Se, and C - S for different compounds are collected in table II.

Attempts have been made by Burmeister and Al-Janabi(30) to prepare new compounds of cobalt (III) and platinum (II) with the  $NCSe$  and  $NCS^-$  ions, but the results have not yet been published. Several new compounds, e.g.,  $Pt(bipy)(SeCN)_2$ ,  $Pt(phen)(SeCN)_2$ ,  $[Co(NH_3)_5NCSe](NO_3)_2$ ,  $K_3[Co(CN)_5NCSe]$ , and

$K_4[(CN)_4Co < \begin{smallmatrix} NCS \\ SCN \end{smallmatrix} > Co(CN)_4] \cdot 4H_2O$  have been reported. The C - N and C - Se stretching frequencies of these compounds are shown in Table III.





Table II

The C-N, C-S, and C-Se Stretching Frequencies in Some Inorganic Thiocyanate and Selenocyanate Compounds ( $\text{cm}^{-1}$ )

| <u>Compounds</u>   | <u><math>\nu_{\text{C-N}}</math></u> | <u><math>\nu_{\text{C-S}}</math></u> | <u><math>\nu_{\text{C-Se}}</math></u> | <u>Ref.</u> |
|--|--------------------------------------|--------------------------------------|---------------------------------------|-------------|
| KSCN   | 2053 s                               | 748 w                                |                                       | 31          |
| KSeCN  | 2070 s                               |                                      | 558 w                                 | 32          |
| $\text{K}_2[\text{Hg}(\text{SCN})_4]$                            | 2115 s                               | 716 w                                |                                       | 21          |
| $\text{K}_2[\text{Hg}(\text{SeCN})_4]$                           | 2098 s                               |                                      | 543 w                                 | 21          |
| $\text{K}_2[\text{Pt}(\text{SCN})_6]$                            | 2125 s                               | 694 w                                |                                       | 33          |
| $\text{K}_2[\text{Pt}(\text{SeCN})_6]$                           | 2124 s                               |                                      | 520 w                                 | 21          |
| $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$           | 2075 s                               |                                      |                                       | 20          |
| $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCSe})_4]$          | 2075 s                               |                                      |                                       | 20          |
| $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$  | 2053 s                               | 840                                  |                                       | 21          |
| $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Co}(\text{NCSe})_4]$ | 2053 s                               |                                      | 672 m                                 | 21          |
| $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$  | 2105 s                               | 820                                  |                                       | 34          |
| $(\text{NH}_4)[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$          | 2110 s                               |                                      |                                       | 22          |
|  | 2042 sh                              |                                      |                                       |             |
| $[(\text{CH}_3)_4\text{N}]_3[\text{Cr}(\text{NCS})_6]$           | 2075 s                               |                                      |                                       | 22          |
|  | 2042 sh                              |                                      |                                       |             |
| $[(\text{CH}_3)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$          | 2067 s                               |                                      |                                       | 22          |
|  | 2041 sh                              |                                      |                                       |             |
| $[\text{Co}(\text{quinoline})_2(\text{NCS})_2]$                  | 2062, 2045                           |                                      |                                       | 20          |
| $[\text{Co}(\text{quinoline})_2(\text{NCSe})_2]$                 | 2070, 2037                           |                                      |                                       | 20          |
| $[\text{Co}(\text{Ph}_3\text{PO})_2(\text{NCS})_2]$              | 2070                                 |                                      |                                       | 20          |
| $[\text{Co}(\text{Ph}_3\text{PO})_2(\text{NCSe})_2]$             | 2066                                 |                                      |                                       | 20          |
| $[\text{Co}(\text{py})_4(\text{NCS})_2]$                         | 2072                                 |                                      |                                       | 20          |
| $[\text{Co}(\text{py})_4(\text{NCSe})_2]$                        | 2073                                 |                                      |                                       | 20          |
| $[\text{Co}(\text{PPh}_3)_2(\text{NCS})_2]$                      | 2040                                 |                                      |                                       | 20          |
| $[\text{Co}(\text{PPh}_3)_2(\text{NCSe})_2]$                     | 2165, 2137                           |                                      |                                       | 20          |
|  | ~ 2070 sh                            |                                      |                                       |             |
| $[\text{Pd}(\text{bipy})(\text{SCN})_2]$                         | 2117(m,sp)                           | 700 w                                |                                       | 26          |
|  | 2108(s,sp)                           |                                      |                                       |             |
| $[\text{Pd}(\text{bipy})(\text{SeCN})_2]$                        | 2116 s                               |                                      | 522.5 w                               | 35          |
|  | 2112 s                               |                                      | 517.5 w                               |             |



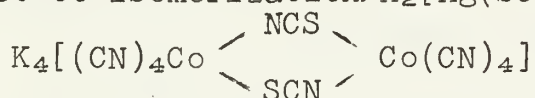
Table III

The C-N and C-Se Stretching Frequencies in Some  
of the New Inorganic Thiocyanate and  
Selenocyanate Compounds ( $\text{cm}^{-1}$ )

| Compound  | $\nu_{\text{C-N}}(\text{cm}^{-1})$ | $\nu_{\text{C-Se}}(\text{cm}^{-1})$ |
|---|------------------------------------|-------------------------------------|
| $[\text{Pt}(\text{bipy})(\text{SeCN})_2]$   | 2130 s,sp<br>2137 sh               | 532 w<br>526.5 w                    |
| $[\text{Pt}(\text{phen})\text{SeCN}]_2$   | 2123, 2131 m                       | 550 w                               |
| $[\text{Co}(\text{NH}_3)_5\text{NCSe}](\text{NO}_3)_2$  | 2070 s,sh<br>2116 vvs              | 623.5 m                             |
| $\text{K}_3[\text{Co}(\text{CN})_5\text{NCSe}]$   | 2070 s<br>2095 w<br>2124, 2127 vvs | 664                                 |
| $\text{K}_4[(\text{CN})_4\text{Co} \begin{array}{c} \diagup \text{NCS} \\ \diagdown \text{SCN} \end{array} \text{Co}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ |                                    | 2120 vvs<br>2180 s,m                |

### CONCLUSION

Although the published results indicate a close similarity in the coordination behavior of the thiocyanate and selenocyanate ions, the most recent work(30) has led to discovery of distinct differences between the two. For example,  $[\text{Pd}(\text{bipy})(\text{SCN})_2]$  readily isomerizes to  $[\text{Pd}(\text{bipy})(\text{NCS})_2]$  whereas  $[\text{Pd}(\text{bipy})(\text{SeCN})_2]$  is stable with respect to isomerization.  $\text{K}_2[\text{Hg}(\text{SCN})_4]$  reacts with  $[\text{Co}(\text{CN})_5]^{3-}$  to form



, whereas, under the same conditions,  $\text{K}_2[\text{Hg}(\text{SeCN})_4]$  reacts with  $[\text{Co}(\text{CN})_5]^{3-}$  to form  $\text{K}_3[\text{Co}(\text{CN})_5\text{NCSe}]$ . No example has yet been found of a coordination complex wherein the normal bonding mode of the selenocyanate ion is changed by the presence of other ligands in the coordination sphere, nor has a steric effect been demonstrated.



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# STRUCTURE OF METAL ALKOXIDES

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July 14, 1964

## INTRODUCTION:

Although metal alkoxides have been known for over a century, it is only in the last ten years that the determination of their structures has been attempted (1). On the basis of chemical and physical properties, there are three distinct groups of metal alkoxides: ionic, giant polymeric, and telemeric. One would intuitively expect the alkoxides of the alkali and alkaline-earth metals to be ionic (2), whereas one would expect those alkoxides which are giant covalent polymers to be the alkoxides of divalent-transition metals, of which all are completely insoluble in organic solvents (3). At present, very little is known of these alkoxides. The third group contains the monomeric and polymeric alkoxides, of which the degree of polymerization is found to vary from two to eight. In Table I, some representative alkoxides are listed together with their respective degrees of polymerization. Most research to date has involved these latter mentioned alkoxides. Bradley has sought to determine the complexity of these alkoxides in solution by applying both cryoscopic and ebulliometric techniques and controlled hydrolysis experiments. During the past three years, x-ray and N.M.R. studies have been made.

TABLE I

Some Representative Alkoxides and their Degree  
of Polymerization

| <u>Compound</u>  | <u>n</u> | <u>Solvent</u>                | <u>Reference</u> |
|--|----------|-------------------------------|------------------|
| TlOCH <sub>3</sub>   | 4.0      | C <sub>6</sub> H <sub>6</sub> | 4                |
| TlOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>  | 4.0      | "                             | 5                |
| Al(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>                     | 4.1      | "                             | 6 *              |
| Al(O <sup>t</sup> Bu) <sub>3</sub>                                   | 1.95     | "                             | 6                |
| Fe(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>                     | 2.9      | "                             | 7                |
| Fe(O <sup>t</sup> Bu) <sub>3</sub>                                   | 1.5      | "                             | 7                |
| Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>                     | 3.0      | "                             | 8 *              |
| Ti(O <sup>t</sup> Bu) <sub>4</sub>                                   | 1.0      | "                             | 8                |
| V(OCH <sub>3</sub> ) <sub>4</sub>                                    | 2.79     | "                             | 9                |
| V(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>                      | 2.04     | "                             | 9                |
| Zr(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>                     | 2.24     | "                             | 10 *             |
| Zr(O <sup>t</sup> Bu) <sub>4</sub>                                   | 1.0      | "                             | 11               |
| Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub>                     | 1.98     | "                             | 12               |
| Ta(O <sup>t</sup> Bu) <sub>5</sub>                                   | 1.01     | "                             | 12               |
| Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub>                     | 2.02     | "                             | 13               |
| Nb(OCHCH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>5</sub> | 1.14     | "                             | 13               |
| U(OC <sub>2</sub> H <sub>5</sub> ) <sub>6</sub>                      | 1.2      | "                             | 14               |
| U(O <sup>t</sup> Bu) <sub>6</sub>                                    | 1.0      | "                             | 14               |

\* Concentration Dependent.

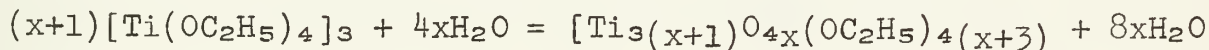




# Results of Cryoscopic, Ebulliometric and Hydrolysis Experiments.

The classical methods for determining the structure of alkoxides are ebulliometry, cryoscopy and controlled hydrolysis experiments. These have been used extensively by Bradley since 1952. Essentially, he has determined the degree of polymerization through cryoscopy and ebulliometry and has assumed that this number--if an integer--corresponds to the number of units per molecule in solution and also in the solid state. From the hydrolysis experiments, in which the complexity is measured as a function of the water added, Bradley (15) has developed a theory which predicts the structure of these alkoxides.

As an example, the hydrolysis experiments with titanium tetroxide (16), which has a degree of polymerization of 3.0 in benzene and 2.91 in ethanol, will be presented. When  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  was hydrolyzed, two different oxide-alkoxide polymers,  $\text{Ti}_6\text{O}_4(\text{OC}_2\text{H}_5)_{16}$  and  $\text{Ti}_9\text{O}_8(\text{OC}_2\text{H}_5)_{20}$ , were isolated at different water/titanium ratios. Assuming that  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  is trimeric in solution, the following equations can be written.



This reaction was studied ebulliometrically, and the observed degree of polymerization,  $n_{\text{obs}}$  was then compared with the value,  $n$ , based on the above model.

If  $h$  = mole ratio of  $\text{H}_2\text{O}/\text{Ti}$

$$h = 4x/3(x+1)$$

$$n = 3(x+1) = 12/4-3h$$

A plot of  $n$  and  $n_{\text{obs}}$  vs  $h$  is shown in Figure 1, and good agreement was found when  $h < 1.0$ . In 1957, Bradley (17) refined this treatment by allowing for the presence of the solvated dimer  $\text{Ti}_2(\text{OC}_2\text{H}_5)_8 \cdot 2\text{C}_2\text{H}_5\text{OH}$ , since in ethanol  $n_{\text{obs}} = 2.91$  for pure  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . The curve for the system  $[\text{Ti}(\text{OC}_2\text{H}_5)_4]_3 + \text{Ti}_2(\text{OC}_2\text{H}_5)_8 \cdot 2\text{C}_2\text{H}_5\text{OH}$  is also plotted on Figure 1 and presents better agreement with the observed data. Because of this agreement, Bradley concluded that  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  is trimeric in solution and titanium is in an octahedral environment. This work, however, has been criticized by Martin and Winters who claim that  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  is a cyclic trimer (18,19). Similar experiments with zirconium alkoxides (10) show that this hydrolysis data can be explained by assuming that these alkoxides are trimeric and have octahedrally coordinated zirconium atoms, and that tantalum alkoxides (20) are dimeric having octahedrally coordinated tantalum atoms.



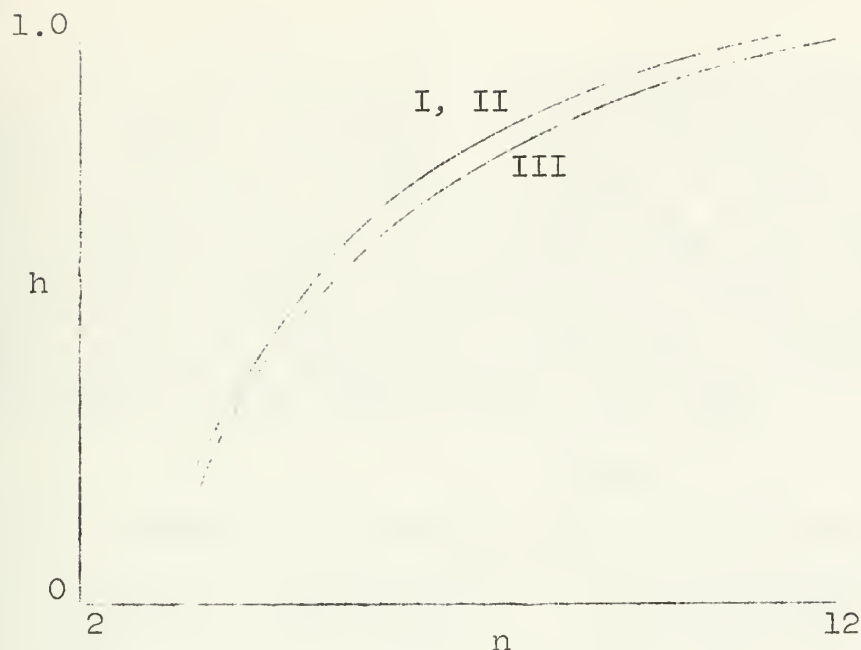


Figure 1.

Plots of the water/titanium mole ratio vs. the degree of polymerization for  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ : I, observed curve; II, calculated curve based on the presence of  $[\text{Ti}(\text{OC}_2\text{H}_5)_4]_3$  and  $\text{Ti}_2(\text{OCH}_2\text{H}_5)_8 \cdot 2\text{C}_2\text{H}_5\text{OH}$ ; III, calculated curve based on the presence of  $[\text{Ti}(\text{OC}_2\text{H}_5)_4]_3$ .

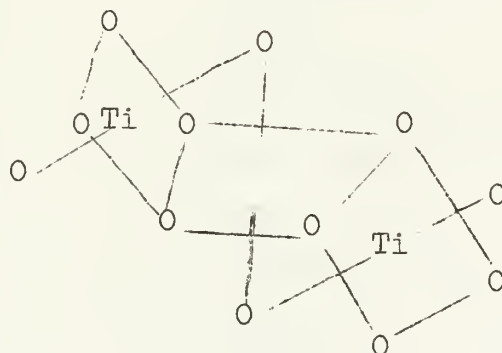


Figure 2.

Structure of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  proposed by Bradley.

O = oxygen in  $\text{OC}_2\text{H}_5$ .



# Structural Theory of Bradley

As a rationalization of the results of the hydrolysis experiments with  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  and of the observed degrees of polymerization found for the various alkoxides, Bradley advanced the following theory (15). Assuming that the coordination number of oxygen does not exceed four, and that the metal alkoxide adopts the smallest possible structural unit consistent with all the metal atoms attaining a higher coordination number through intermolecular bonding, then the stereochemistry of the metal atom can be predicted if the degree of polymerization is known. This is represented in Table II. Only for the aluminum alkoxides does he encounter difficulty in correlating this theory with the cryoscopic and ebulliometric data (21).

TABLE II

Degree of Polymerization as a Function of Stereochemistry

| Compound                  | Coordination<br>No. of M | Stereochemistry<br>of M    | Minimum Degree of<br>Polymerization |
|---------------------------|--------------------------|----------------------------|-------------------------------------|
| MOR                       | 2                        | OMO = $90^\circ$           | 2                                   |
|                           | 2                        | OMO = $120^\circ$          | 3                                   |
|                           | 3                        | pyramidal                  | 4 *                                 |
| $\text{M}_2(\text{OR})_2$ | 3                        | planar-one OMO= $90^\circ$ | 2                                   |
|                           | 3                        | planar OMO = $90^\circ$    | 3                                   |
|                           | 4                        | tetrahedral                | 3                                   |
|                           | 4                        | planar                     | 4                                   |
|                           | 6                        | octahedral                 | >                                   |
| $\text{M}(\text{OR})_3$   | 4                        | tetrahedral                | 2 *                                 |
|                           | 4                        | planar                     | 2                                   |
|                           | 6                        | octahedral                 | 8 *                                 |
| $\text{M}(\text{OR})_4$   | 5                        | trigonal bipyramidal       | 2                                   |
|                           | 6                        | octahedral                 | 3 *                                 |
|                           | 8                        | cubic                      | 8                                   |
| $\text{M}(\text{OR})_5$   | 6                        | octahedral                 | 2 *                                 |
|                           | 8                        | cubic                      | 4                                   |
| $\text{M}(\text{OR})_6$   | 8                        | cubic                      | 2 *                                 |

\* Prediction of Theory



1. The first part of the report is a summary of the work done during the year. It includes a list of the projects completed, a description of the work done on each project, and a summary of the results of the work. The second part of the report is a detailed description of the work done on each project. This includes a description of the objectives of the project, a description of the methods used, and a description of the results of the work. The third part of the report is a summary of the work done during the year. This includes a list of the projects completed, a description of the work done on each project, and a summary of the results of the work.

# Summary

The following table shows the results of the work done during the year.

| Project    | Objectives  | Methods   | Results   |
|------------|---|---|---|
| Project 1  | 1. To determine the effect of temperature on the rate of reaction.          | 1. To determine the effect of temperature on the rate of reaction.          | 1. To determine the effect of temperature on the rate of reaction.          |
| Project 2  | 2. To determine the effect of concentration on the rate of reaction.        | 2. To determine the effect of concentration on the rate of reaction.        | 2. To determine the effect of concentration on the rate of reaction.        |
| Project 3  | 3. To determine the effect of catalyst on the rate of reaction.             | 3. To determine the effect of catalyst on the rate of reaction.             | 3. To determine the effect of catalyst on the rate of reaction.             |
| Project 4  | 4. To determine the effect of surface area on the rate of reaction.         | 4. To determine the effect of surface area on the rate of reaction.         | 4. To determine the effect of surface area on the rate of reaction.         |
| Project 5  | 5. To determine the effect of pressure on the rate of reaction.             | 5. To determine the effect of pressure on the rate of reaction.             | 5. To determine the effect of pressure on the rate of reaction.             |
| Project 6  | 6. To determine the effect of light intensity on the rate of reaction.      | 6. To determine the effect of light intensity on the rate of reaction.      | 6. To determine the effect of light intensity on the rate of reaction.      |
| Project 7  | 7. To determine the effect of pH on the rate of reaction.                   | 7. To determine the effect of pH on the rate of reaction.                   | 7. To determine the effect of pH on the rate of reaction.                   |
| Project 8  | 8. To determine the effect of solvent on the rate of reaction.              | 8. To determine the effect of solvent on the rate of reaction.              | 8. To determine the effect of solvent on the rate of reaction.              |
| Project 9  | 9. To determine the effect of ionic strength on the rate of reaction.       | 9. To determine the effect of ionic strength on the rate of reaction.       | 9. To determine the effect of ionic strength on the rate of reaction.       |
| Project 10 | 10. To determine the effect of dielectric constant on the rate of reaction. | 10. To determine the effect of dielectric constant on the rate of reaction. | 10. To determine the effect of dielectric constant on the rate of reaction. |

## X-Ray Determination of Structures

Complete x-ray structure determinations would naturally be most desirable for elucidating the structure of these polymeric alkoxides; however, the structures of only four alkoxides have been determined by this method. The crystal structure of thallous methoxide (22), which was known to be tetrameric in benzene (4), was found to be a tetramer in the solid state. Ibers (23) determined the crystal structure of titanium tetraethoxide and has found it also to be tetrameric, whereas in benzene solution it is trimeric. Wheatley (2,24) has determined the structure of lithium methoxide, and, as expected, this compound is ionic having the same structure, a layer type, as lithium hydroxide (25). In  $\text{LiOCH}_3$ , the  $\text{Li-O}$  bond distance is 1.95 Å as compared with a similar distance, 1.96 Å, in  $\text{LiOH}$ . It is worthwhile to mention briefly the crystal structure of the related mercury(II) methylmercaptide,  $\text{Hg}(\text{SCH}_3)_2$  (26). Each mercury atom is covalently bonded to two sulfur atoms at a distance of 2.36 Å and weakly bonded to three other sulfur atoms at a distance of 3.25 Å. The intermolecular bonding through the mercaptide sulfur atoms causes a large polymeric molecule in which each mercury atom has an irregular tetragonal pyramidal environment.

A different technique, N.M.R., has been applied to this problem only in the related sillyoxide system (27). The trimethylsilyloxides of aluminum and gallium, which have degrees of polymerization of two in benzene, have proton spectra containing two bands, thus corresponding to a dimeric structure with bridging sillyoxide groups. The trimethylsilyloxiide of boron, which is monomeric in benzene, has a proton spectrum containing only one band.

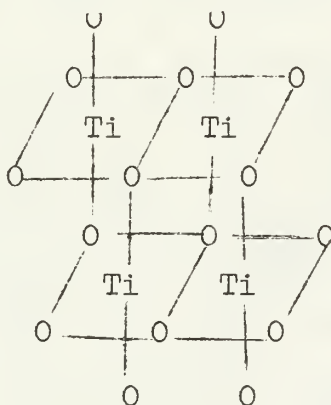


Figure 3.

Crystal Structure of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$

O = oxygen in  $\text{OC}_2\text{H}_5$



## Conclusion

The structural data presented has been of two types. From the cryoscopy, ebulliometry and hydrolysis experiments degrees of polymerization have been determined and the structures of various alkoxides have been inferred. The structural theory of Bradley is based solely on this type of data. The second type which is x-ray data, presents direct structural evidence and can be used to evaluate Bradley's theory.

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THE ELECTRONIC STRUCTURES OF COPPER(II) ACETATE  
and RELATED COMPOUNDS

Michael F. Rettig

July 21, 1964

INTRODUCTION

Copper(II) ion, which has a  $d^9$  electronic configuration, usually shows a room temperature magnetic moment in the range 1.9-2.2 B.M., corresponding to one unpaired electron with appreciable contribution from spin-orbit coupling. However, in 1915, Lifschitz and Rosenbohm(1) observed that the room temperature moment of copper(II) acetate monohydrate is anomalously low, being about 1.4 B.M. Since that time, much experimental and theoretical work has been done on  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  and related compounds.(2) The general picture which emerges is that in certain instances two copper(II) ions are held together by four bridging groups, forming a binuclear complex. This circumstance gives short copper-copper distances, and "metal-metal" interaction. Several groups of theoretical chemists have attempted to elucidate the mechanism of this "metal-metal" interaction. One thing seems clear and should be stated at the outset: the "metal-metal" interaction in binuclear copper(II) compounds is weak, and it is not expected that a dimer would form on the basis of this interaction alone. Rather, it seems more reasonable to consider the "metal-metal" interaction to be a result, not a cause, of dimerization.

The purpose of this seminar is threefold: 1) the experimental data pertinent to a discussion of the electronic structure of  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  will be reviewed; 2) several approximate treatments of the bonding in  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  will be outlined and discussed in the light of the experimental data; and 3) some binuclear compounds related to  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  will be briefly described.

EXPERIMENTAL RESULTS

Magnetic Susceptibility Studies: Table I summarizes the important magnetic results for solid samples.

# THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth and change. It begins with the first settlers, who came to the Americas in search of a new life. They found a land of opportunity, but also one of hardship. The early years were marked by struggle and sacrifice, as the settlers fought to establish a new society. Over time, the United States grew from a small colony into a powerful nation. It was a process of constant evolution, shaped by the dreams and aspirations of its people. The story of the United States is a testament to the power of the human spirit and the ability to overcome adversity.

The United States has a rich and diverse heritage. It is a land of many cultures, languages, and traditions. This diversity is one of its greatest strengths, as it has allowed the nation to embrace change and innovation. The history of the United States is a story of resilience and perseverance, of a people who have built a great nation from the ground up. It is a story that continues to inspire and guide us today.

THE HISTORY OF THE UNITED STATES

Table I

## Magnetic Behavior of Some Solid Copper(II) Alkanoates

| Compound   | Temp. (K) | T <sub>c</sub> (K) | - J (cm <sup>-1</sup> ) | g        | (B.M.) <sup>a</sup> | Ref |
|--|-----------|--------------------|-------------------------|----------|---------------------|-----|
| [Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>                                      | 90°-400°  | 270°               | 302                     | 2.17     | 1.39                | 4   |
| [Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> OH] <sub>2</sub>                                    | 90°-400°  | 255°               | 286                     | 2.13     | 1.41                | 3,4 |
| [Cu(RCO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> and b)  | 90°-400°  | 278°±28°           | 309±31                  | 2.15±.08 | 1.35-1.41           | 5   |
| [Cu(RCO <sub>2</sub> ) <sub>2</sub> OH] <sub>2</sub> <sup>c</sup>                                      |           | 500°               | 550                     | 2.16     | 0.96-1.10           | 7   |
| [Cu(HCO <sub>2</sub> ) <sub>2</sub> L <sub>n</sub> ] <sub>2</sub> <sup>c</sup>                         | 85°-370°  | 298°±9°            | 329±8                   | 2.27±.05 | 1.34-1.40           | 8   |
| [Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> L] <sub>2</sub> <sup>d</sup>                        | 94°-350°  | 300°±5°            | 333±9                   | 2.21±.03 | 1.32-1.37           | 8   |
| [Cu(C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>2</sub> L] <sub>2</sub> <sup>d</sup>          | 94°-350°  | 97°±6°             | 112±12                  | 2.18±.00 | 1.73-1.76           | 8   |
| [Cu(C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>2</sub> L] <sub>2</sub> <sup>e</sup>          |           |                    |                         |          |                     |     |
| [Cu(C <sub>1</sub> CH <sub>2</sub> CO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> n] <sub>2</sub>    | -----     | -----              | --                      | ----     | 1.42-1.74           | 10  |
| and [Cu(C <sub>1</sub> CHCO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> n] <sub>2</sub> <sup>f</sup> |           |                    |                         |          |                     |     |
| [Cu(C <sub>1</sub> CO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> <sup>g</sup>                          | -----     | -----              | --                      | ----     | 1.77                | 10  |
| [Cu(C <sub>1</sub> CO <sub>2</sub> ) <sub>2</sub> OH] <sub>2</sub> <sup>g</sup>                        | -----     | -----              | --                      | ----     | 1.89                | 10  |

<sup>a</sup> measured at room temperature; <sup>b</sup> R is propionate, butyrate, laurate, stearate, or behenate.

<sup>c</sup> Results are stated as mean ± mean deviation of results for all compounds in the series;

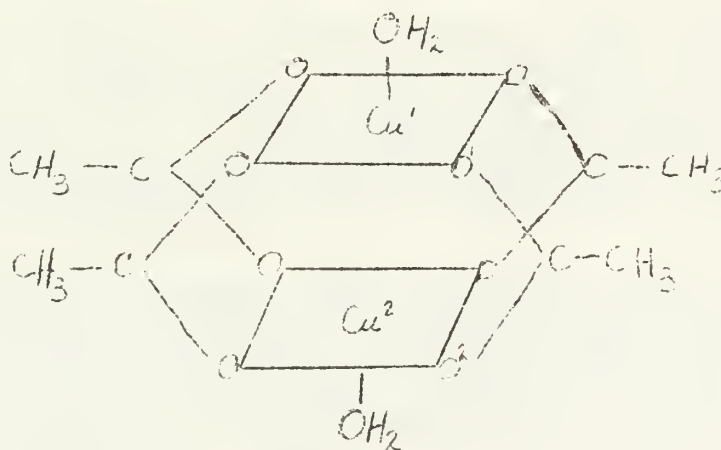
n = 1 for pyridine, <sup>v</sup>-, <sup>h</sup>-, <sup>i</sup>-picoline, and n = 1/2 for dioxane; L is nothing, water, pyridine, <sup>v</sup>-, <sup>h</sup>-, or <sup>x</sup>-picoline; <sup>e</sup>L is aniline, p- or m-toluidine; n is zero or 4, result is range of observed values; <sup>g</sup> may or may not be binuclear (x unknown)



It was found that the magnetic moments of the copper(II) alkanoates in benzene or dioxane solution are nearly the same as those of the solids.(6) Kondo and Kubo(9) determined the room temperature magnetic moment of copper(II) acetate in various solvents. The results are as follows: methanol (1.58 B.M.); ethanol (1.43 B.M.); dioxane (1.37 B.M.). These moments are subnormal, and it was concluded that the binuclear structure persists in methanol, ethanol, and dioxane.

Electron Spin Resonance: Bleaney and Bowers(11) determined the ESR parameters for single crystals of  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\cdot\text{OH}_2]_2$ . It was found that the "paramagnetic units" in the unit cell behave as would a species of spin  $S = 1$ . In other words, pairs of copper(II) ions are so situated in the unit cell that the unpaired spins of each copper(II) ion are strongly coupled. The intensity of the resonance lines decreased with a decrease in temperature and, at  $20^\circ\text{K}$ , no spectrum was observed. This was interpreted to mean that the triplet state is less stable than the singlet, and only through thermal excitation is the triplet occupied above  $20^\circ\text{K}$ . Bleaney and Bowers obtained  $g_{\perp} = 2.08 \pm .03$  and  $g_{\parallel} = 2.42 \pm .03$  at  $90^\circ\text{K}$ . Later Abe and Shimada(12) reported  $g_x = 2.05$ ,  $g_y = 2.09$  and  $g_z = 2.34$  for  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\cdot\text{OH}_2]_2$  at  $300^\circ\text{K}$ .

X-Ray Structure Determinations: An x-ray structure determination has been done for  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\cdot\text{OH}_2]_2$ .(13) The main features of the structure are shown in Figure 1. Note the short copper-copper distance and that the four oxygen atoms lie  $0.22 \text{ \AA}$  below the plane of the copper(II) ion. It was considered that the short copper-copper distance must lead to a "metal-metal" bond, but the authors did not elaborate.(13)



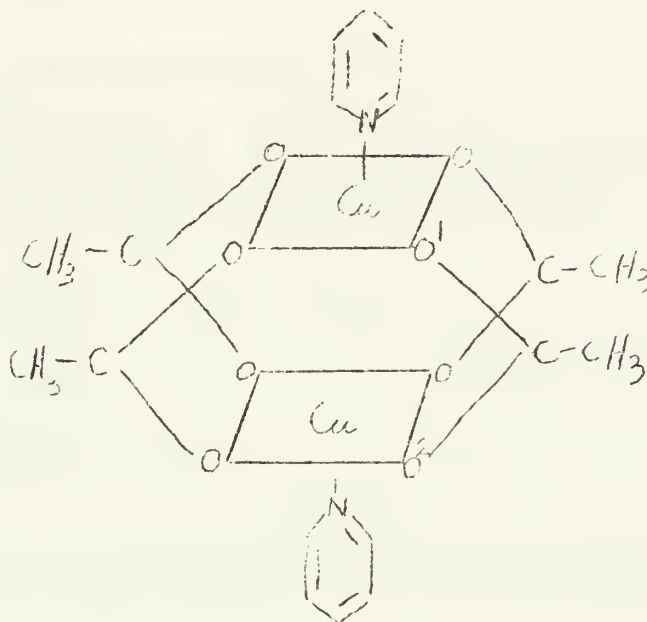
$\text{Cu}-\text{OH}_2 (2.20 \text{ \AA})$ ;  $\text{C}-\text{O} (1.33 \text{ \AA})$ ;  $\text{Cu}-\text{Cu} (2.64 \text{ \AA})$ ;  $\text{O}^1-\text{O}^2 (2.20 \text{ \AA})$ ;  
 $\text{Cu}-\text{O}^1 (1.97 \text{ \AA})$ ;  $\angle \text{O}^1-\text{C}-\text{O}^2 (112^\circ)$ ;  $\angle \text{O}^1-\text{Cu}^1-\text{Cu}^2 (83^\circ)$ .

Figure 1





The crystal structure of  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{C}_5\text{H}_5\text{N}]_2$  has been determined.(14) This structure is shown in Figure 2.



$\text{Cu}-\text{O}^1(1.98 \text{ \AA})$ ;  $\text{Cu}-\text{N}(2.12 \text{ \AA})$ ;  $\text{C}^1-\text{O}^2(1.24 \text{ \AA})$ ;  $\text{Cu}-\text{Cu}(2.63 \text{ \AA})$ ;  $\text{O}^1-\text{O}^2(2.20 \text{ \AA})$ ;  $\angle \text{O}^1-\text{C}-\text{O}^2(125^\circ)$ . The angle between the planes of the pyridine rings is  $60^\circ$ .

Figure 2

The structure of a second crystal modification of  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{C}_5\text{H}_5\text{N}]_2$  has also been reported(15,48) There are two important differences between this structure and that shown in Figure 2: 1) the copper-copper distance is  $2.70 \text{ \AA}$ ; 2) the pyridine rings lie in the same plane. A rationalization of these differences has not been advanced, but the effects may arise from pi-bonding.

Absorption Spectra: Both polarized single crystal and solution spectra are available for copper(II) acetate and certain of its derivatives. Compounds having the binuclear structure absorb in the range  $7000-7500 \text{ \AA}$  ( $13,300-14,300 \text{ cm}^{-1}$ ) and have another band (considered to be diagnostic of copper-copper interaction) at  $3750 \text{ \AA}$  (ca.  $27,000 \text{ cm}^{-1}$ ). The former band is x,y polarized while the latter is z polarized.(16,17) Low temperature polarized spectra for  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  have been determined.(19) Solution spectra for compounds of the type  $[\text{Cu}(\text{RCO}_2)_2\text{L}]_2$  show an insensitivity to the nature of the R group(20,21), while variations of L lead to more pronounced shifts.(21,8) Graddon(22,23,46) concluded that the copper(II) acetate spectrum is typical of penta-coordinate copper(II),

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and that the 3750 Å band is not necessarily diagnostic of metal-metal interaction.

# THEORETICAL INTERPRETATIONS

[Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>OH<sub>2</sub>]<sub>2</sub> was discussed qualitatively by Figgis and Martin in 1956.(4) These authors based their argument on the energy level scheme given by Polder,(25) shown in Figure 3. The bonding interaction was postulated to arise

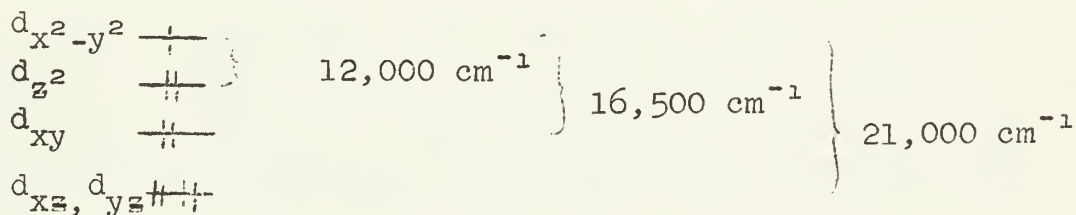


Figure 3

from  $d_{x^2-y^2} - d_{x^2-y^2}$  overlap, as shown in Figures 4 and 5.

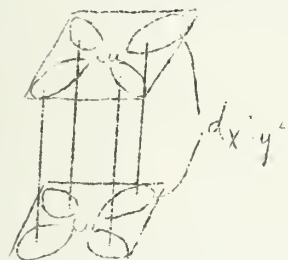


Figure 4

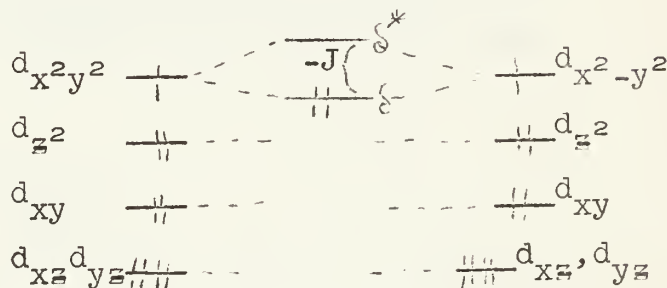


Figure 5

As indicated in Figure 5, the bonding electrons occupy an orbital of  $\delta$  symmetry, and the bond is described as a "delta-bond." The authors considered that the two highest energy levels are  $\delta$  and  $\delta^*$ , and they did not specify the interactions among remaining d-orbitals. In this model, the energy difference between the states  $(\delta)^2(\delta^*)^0$  and  $(\delta)^1(\delta^*)^1$  corresponds to the experimentally determined singlet-triplet splitting,  $-J$ . A  $\sigma$ -bonded model, where the highest unoccupied level is derived from  $d_{z^2} d_{z^2}$  interaction, was rejected as being energetically unfavorable.

In 1959, Ross(26) gave a more detailed account of the bonding in [Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>OH<sub>2</sub>]<sub>2</sub>. Using valence bond and crystal field theory, he obtained the scheme shown in Figure 6. This

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Figure 6

more detailed treatment agreed with the earlier description in terms of a "delta-bond".(4) Ross rejected a possible alternative description in terms of  $\sigma$ -bonding by comparing predicted and observed g-values. Ross and Yates(27) showed that the singlet-triplet splitting calculated for the "delta-bonded" model could be brought into agreement with the experimental value of  $-J$ .

In 1962, Forster and Ballhausen(18) discussed  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\cdot 2\text{OH}_2]_2$  from an LCAO-MO viewpoint. These investigators used the Stark splitting pattern derived previously by Holmes and McClure(28) for copper(II) ion (Figure 7) in order to obtain their LCAO-MO Scheme (Figure 8). The empty

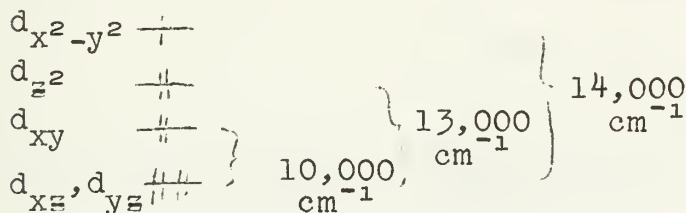


Figure 7

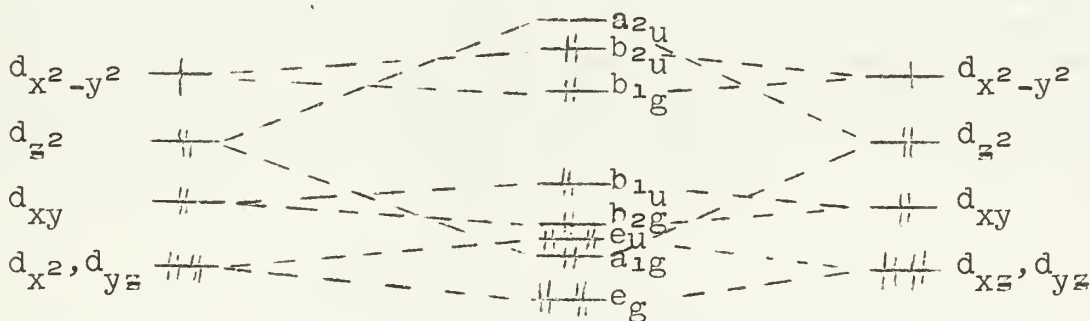


Figure 8  
(not drawn to scale)

The first part of the paper is devoted to a study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \sum_{n=0}^{\infty} \frac{f_n(x)}{n!}$ , where  $f_n(x)$  is a function of the  $n$ -th order of the differential equation  $y^{(n)} = P_{n-1}(x)y^{(n-1)} + \dots + P_0(x)y$ .

In the second part of the paper, we shall study the properties of the function  $f(x)$  defined by the equation  $f(x) = \sum_{n=0}^{\infty} \frac{f_n(x)}{n!}$ , where  $f_n(x)$  is a function of the  $n$ -th order of the differential equation  $y^{(n)} = P_{n-1}(x)y^{(n-1)} + \dots + P_0(x)y$ .

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The sixth part of the paper is devoted to a study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \sum_{n=0}^{\infty} \frac{f_n(x)}{n!}$ , where  $f_n(x)$  is a function of the  $n$ -th order of the differential equation  $y^{(n)} = P_{n-1}(x)y^{(n-1)} + \dots + P_0(x)y$ .

$a_{2u}$  molecular orbital implies that any net stabilization arises from a  $d_{z^2}-d_{z^2} \sigma$ -bond, in contrast to the earlier described  $\delta$ -bond.(4,26)

Tonnet, Yamada, and Ross(19) have compared the valence bond and LCAO-MO descriptions, and have reaffirmed the  $\delta$ -bonded model.

Boudreaux(29) gave a second molecular orbital description of  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$ , using what he felt was a more realistic Stark splitting for the d-levels. This scheme is shown in Figure 9. Boudreaux' results indicate a  $\sigma$ -bond, as did

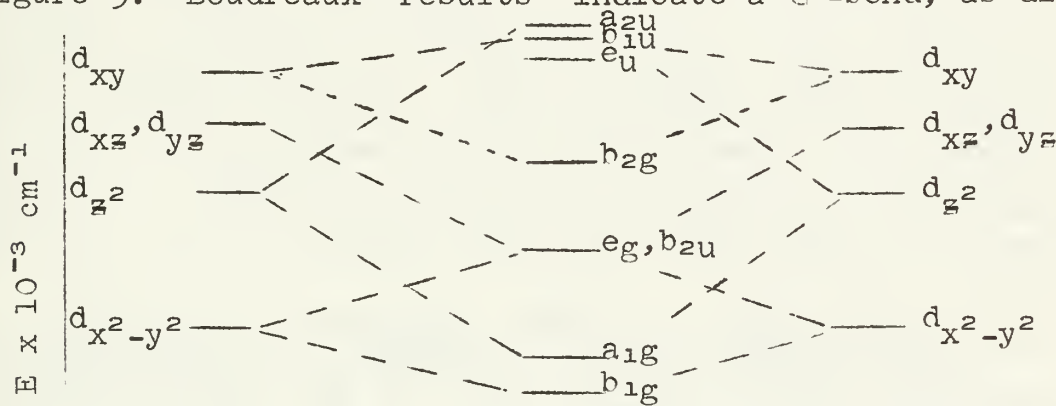


Figure 9

the earlier MO description.(18) Further, this scheme was found to be consistent with several experimental parameters, as will be discussed in seminar.

Magnetic coupling by Kramers' superexchange mechanism (30,49-54) has received little attention in connection with the present problem. This mechanism involves spin coupling of magnetic ions through the agency of intervening non-magnetic groups. Superexchange apparently operates in antiferromagnetic  $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (31, Figure 10) It has been generally felt that the short copper-copper distance in the binuclear

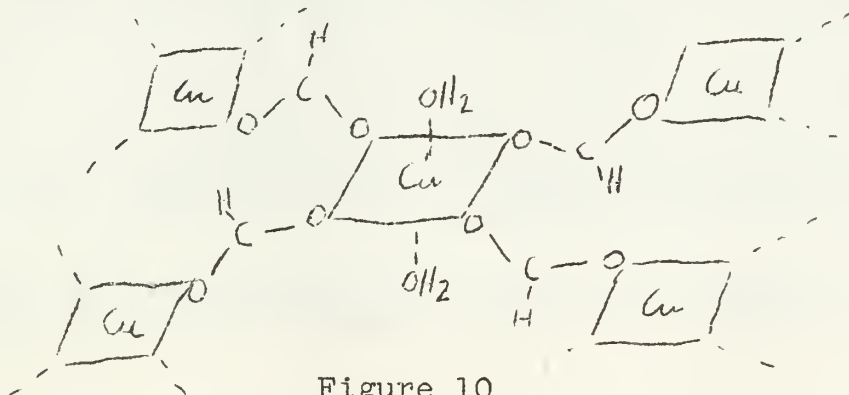


Figure 10

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compounds favors the direct mechanism, but the superexchange mechanism, it would appear, has not been ruled out either theoretically or experimentally.

## RELATED SYSTEMS

Rhodium (II) Carboxylates: The structure of diamagnetic (24)  $[\text{Rh}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  has been determined by x-ray methods. (33) This compound is isostructural with  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$ , the rhodium-rhodium distance being  $2.45 \text{ \AA}$ . The magnetic behavior is clearly anomalous, since rhodium(II) is a  $d^7$  ion, and should be paramagnetic. Anhydrous  $[\text{Rh}(\text{CH}_3\text{CO}_2)_2]_2$  as well as adducts with the following ligands have been prepared (34):  $\text{H}_2\text{O}$ , tetrahydrofuran,  $\text{CH}_3\text{CN}$ , dimethylsulfoxide,  $(\text{CH}_3)_2\text{S}$ ,  $(\text{CH}_3)_3\text{N}$ ,  $\text{CH}_3\text{COOH}$ , pyridine,  $\text{NH}_3$ ,  $\text{NO}$ , ethylenediamine and o-phenanthroline. Infrared spectra were used to infer that the anhydrous acetate and adducts are binuclear. Absorption spectra and extinction coefficients were reported for this series, but there seems to be no magnetic data. (34) Also,  $[\text{Rh}(\text{CF}_3\text{CO}_2)_2]_2$  and some adducts were prepared. (34)

Chromium (II) Acetate: Anhydrous chromium(II) acetate and the monohydrate are diamagnetic at room temperature. (35)  $[\text{Cr}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  was found to be isostructural with  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$ . (36,37) The chromium-chromium distance is  $2.64 \text{ \AA}$ , and this was taken as evidence for "direct interaction" of the metal ions. Chromium(II) is a  $d^4$  ion, and it is possible that the electrons are paired in single ion orbitals. Of course it is also possible that the spins are paired in molecular orbitals. Furlani (38) has discussed  $[\text{Cr}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  from the electrostatic crystal field viewpoint.

Other Carboxylates: Molybdenum(II) and rhenium(III), both  $d^4$  ions, were found to form diamagnetic carboxylates. (39,40) It was shown (40) that the rhenium(III) species are dimeric in solution, having the formula  $[\text{Re}(\text{RCO}_2)_2\text{Cl}]_2$ , and the workers pointed out that "it is not necessary to invoke metal-metal bonding to account for the diamagnetism." (cf. above)

Bridging Atoms Other Than Oxygen: Nortia (41) observed that red cupric thioacetate is diamagnetic at room temperature, with absorption bands at  $3750 \text{ \AA}$  ( $28,000 \text{ cm}^{-1}$ ) and  $5400 \text{ \AA}$  ( $18,000 \text{ cm}^{-1}$ ). These bands were compared to the bands in  $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$  which appear at  $28,000 \text{ cm}^{-1}$  and  $14,000 \text{ cm}^{-1}$  in the reflectance spectrum. It was suggested (41) that the shift to  $18,000 \text{ cm}^{-1}$  in the thioacetate arises from increased tetragonality in the crystal field. Nyholm (42) gave a tentative rationalization of the magnetic differences in the thioacetate and the acetate.

A very interesting series of complexes is formed by deprotonated 1,3-diphenyltriazene (Figure 11). Harris and Martin (43)





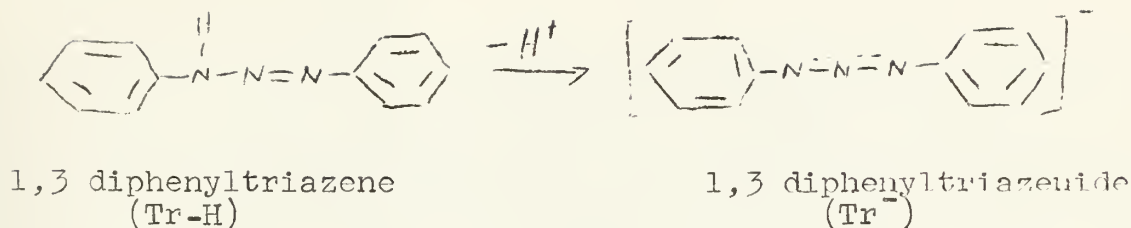


Figure 11

obtained the dark green  $[\text{CuTr}_2]_2$ . This compound is diamagnetic in the solid state from 80°K - 400°K., and is dimeric and diamagnetic in benzene solution.  $[\text{CuTr}_2]_2$  shows a broad absorption band centered at about 6250 Å. Figure 12 shows the structure of  $[\text{CuTr}_2]_2$ , assigned on the basis of the foregoing evidence.

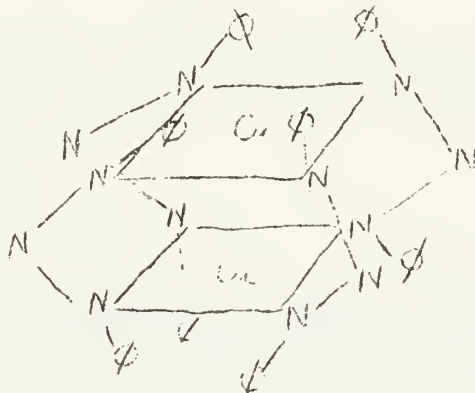


Figure 12

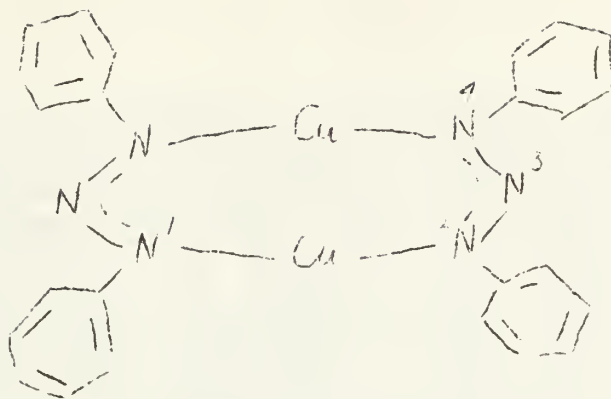
The anomalous magnetic behavior of  $[\text{CuTr}_2]_2$  was considered to arise from direct metal-metal interaction.(43) It will be observed that the spin pairing here is stronger than in the copper(II) alkanoates. The investigators considered(44) that the dimeric, diamagnetic compounds  $[\text{NiTr}_2]_2$  and  $[\text{PdTr}_2]_2$  are isostructural with  $[\text{CuTr}_2]_2$ .  $[\text{Co(II) Tr}_2]_2$  has been reported to have a magnetic moment of 2.1 B.M. at room temperature.(45) The electronic spectra of  $[\text{CuTr}_2]_2$ ,  $[\text{NiTr}_2]_2$ , and  $[\text{CoTr}_2]_2$  were recorded.(45) Graddon(46) mathematically resolved the visible peak of  $[\text{CuTr}_2]_2$  into Gaussian components at 15,000  $\text{cm}^{-1}$  and 19,000  $\text{cm}^{-1}$  (a band near 27,000  $\text{cm}^{-1}$  is obscured by charge transfer absorption). He concluded that  $[\text{CuTr}_2]_2$  shows a typical tetracoordinate copper(II) spectrum. It appears that no crystal structures have been determined for compounds of the type  $[\text{M(II)Tr}_2]_2$ . However, the structure of  $[\text{Cu(I)Tr}]_2$  has been determined by x-ray methods,(47) and is shown in Figure 13.

The first part of the paper is devoted to a discussion of the general principles of the theory of the structure of the atom. It is shown that the structure of the atom is determined by the laws of quantum mechanics, and that the laws of quantum mechanics are determined by the laws of the special theory of relativity.

In the second part of the paper, the author discusses the question of the structure of the nucleus. It is shown that the structure of the nucleus is determined by the laws of quantum mechanics, and that the laws of quantum mechanics are determined by the laws of the special theory of relativity.

The third part of the paper is devoted to a discussion of the question of the structure of the molecule. It is shown that the structure of the molecule is determined by the laws of quantum mechanics, and that the laws of quantum mechanics are determined by the laws of the special theory of relativity.

The fourth part of the paper is devoted to a discussion of the question of the structure of the crystal. It is shown that the structure of the crystal is determined by the laws of quantum mechanics, and that the laws of quantum mechanics are determined by the laws of the special theory of relativity.



$\angle N^1-Cu-N^2(172^\circ)$ ;

$Cu-Cu(2.45 \text{ \AA})$ ;  $N^2-N^3(1.316 \text{ \AA})$ ;  $N^3-N^4(1.274 \text{ \AA})$ ;  $Cu-N^4(1.92 \text{ \AA})$

Figure 13

With small deviations, all the atoms in this molecule lie in the same plane. The ability of  $Tr^-$  to bridge two metal ions is thus established.

## CONCLUSIONS

The diversity of opinion regarding the mechanism of the "metal-metal" interaction in copper(II) alkanoates indicates that more work, both theoretical and experimental, is needed. Probably one of the more fruitful lines of research would involve assignments of electronic transitions in tetra- and pentacoordinate copper(II), inasmuch as any theoretical treatment of the bonding in copper(II) complexes must begin with a Stark splitting pattern for the d-levels. The effects of  $\sigma$ - and  $\pi$ -covalency in copper(II) alkanoates should be experimentally studied, in order that the theoretical models might be more complete. It is probable that other binuclear complexes will provide experimental information pertinent to the problem. Finally, the importance of Kramers' superexchange in binuclear complexes bridged by more than one atom should be assessed.



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The first part of the paper is devoted to a general discussion of the problem. It is shown that the problem is of great importance in the theory of differential equations. The second part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The third part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The fourth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The fifth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The sixth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The seventh part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The eighth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The ninth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The tenth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem.



# THE USE OF HIGH-SURFACE-AREA-SILICA GELS FOR OBSERVING AND MEASURING ION-SOLVATION

Kenneth C. Williams

July 28, 1964

One of the difficult problems encountered in the study of electrolyte solutions is the nature of ion-solvent interactions. In order to understand and describe these solutions in detail, several questions need to be answered. Does the bare ion exist in solution or does it carry with it solvent molecules sufficiently bound to be regarded as part of the ion? If solvent molecules are firmly bound, how many such molecules are "attached"?

The importance of the above questions is realized when notice is taken of the various methods which have been used to study and measure ion-hydrate radii. Some of these methods are theoretical calculations (1), freezing point lowering (2), density and viscosity measurements (3), partial molal volumes (4), compressibility of electrolytic solutions (5), isotopic exchange (6), conductance and diffusion (7), geometric effects at the solution-surface interface (8,9,10,11).

In this seminar, the last two methods will be discussed with emphasis on the last method cited.

## CONDUCTANCE AND DIFFUSION

The transport processes of conductance and diffusion are unique in providing ionic parameters directly from experimental measurements. By means of the relations of G. G. Stokes and of Stokes and Einstein, the radii of migrating or diffusing species may be calculated using the equation given by Nightingale (7):

$$r_s = 0.820 z / \lambda^{\circ} \eta^{\circ} = 0.732 \times 10^{-9} T/D^{\circ}, \quad (1)$$

where  $z$  is the absolute charge of the ion,  $\lambda^{\circ}$  is the limiting ionic equivalent conductance,  $\eta^{\circ}$  is the viscosity of the solvent,  $T$  is the absolute temperature, and  $D^{\circ}$  is the limiting ionic diffusion coefficient. However, Stokes' law radii, which are calculated from limiting equivalent conductances, are often inappropriately small because water is not a continuous medium and because the radii of the water molecules usually are not sufficiently large compared with that of the hydrated ions for the conditions of viscous flow to be fulfilled. In order to measure effectively the deviations from Stokes' law for small ions, Nightingale established a calibration procedure based upon ions whose radii in solution are known and, consequently, upon the crystal radii of ions which are unhydrated. By assuming that the large tetraalkylammonium ions possess a sufficiently small surface charge density to be unhydrated, he prepared a calibration curve by plotting  $r_x/r_s$  vs.  $r_s$ , where  $r_x$  is the crystal ionic radius and  $r_s$  is the Stokes' radius of the tetraalkylammonium ions. The radii obtained by Nightingale for many ions are given in Table 1 for comparison to values obtained by the following method.



THE UNIVERSITY OF CHICAGO  
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RESEARCH REPORT NO. 1000

The following is a summary of the results of the experiments conducted during the past year. The work was carried out in the laboratory of Professor J. H. Goldstein, and the results are presented in the form of a report to the Department of Chemistry. The experiments were designed to determine the effect of temperature on the rate of reaction of hydrogen peroxide with various organic compounds. The results show that the rate of reaction increases with increasing temperature, and that the effect is more pronounced for certain compounds than for others. The data are presented in the following table:

| Compound     | Rate of Reaction at 25°C. | Rate of Reaction at 35°C. | Rate of Reaction at 45°C. |
|--------------|---------------------------|---------------------------|---------------------------|
| Hydroquinone | 0.12                      | 0.25                      | 0.45                      |
| Resorcinol   | 0.15                      | 0.30                      | 0.55                      |
| Catechol     | 0.18                      | 0.35                      | 0.65                      |
| Phenol       | 0.20                      | 0.40                      | 0.75                      |

The results of the experiments are in good agreement with the theoretical predictions, and they show that the rate of reaction of hydrogen peroxide with organic compounds is highly sensitive to temperature. The data also indicate that the effect of temperature is more pronounced for compounds which are more easily oxidized. The work was supported by the National Science Foundation, and the results are being published in the Journal of Organic Chemistry.

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## GEOMETRIC EFFECTS AT THE SOLUTION-SURFACE INTERFACE

### Introduction

If, in solution, two species of different radii are allowed to come in contact with a high-surface-area silica gel, an increase in concentration of the larger species will occur in the bulk solution (providing reaction with surface is prevented). This is due to a geometric effect which occurs whenever spheres of unequal size contact a surface. This phenomenon has been observed in several systems (12, 8, 13, 9, 11) but in some systems was not recognized (14, 15, 16).

### Calculation of Size

If  $V_A$  and  $V_B$  are the volumes available to the smaller (solvent) and larger (ion-hydrate) species, respectively, and  $c_i$  is the concentration of the larger species in a boundless system, and  $c_f$  the concentration after contact with the surface then (11)

$$\frac{c_i}{c_f} = \frac{V_B}{V_A} \quad (2)$$

The pores of the silica gel are assumed to be cylindrical so that the volume available to the larger species is

$$V_B = V_A - P_A W + W \pi \sum_j l_j (r_j - r_B)^2$$

where the pore size distribution is approximated by a series of pores of length  $l_j$  and radius  $r_j$ , with  $r_j > r_B$ , and where  $V_A$  is the volume of solution mixed with weight  $W$  of gel whose pore volume per unit weight (the volume species A penetrates) is  $P_A$ . For a weight  $W$  of gel, the summation term represents the volume inside the pores available to species B, and the term  $V_A - P_A W$  represents the volume outside the pores. The pore volume per unit weight available to species A in the  $j$ th pore is given by equation (4).

$$P_{Aj} = \pi l_j (r_j - r_A)^2, \quad (4)$$

where  $r_j > r_A$ . Determination of the pore volume distribution as a function of pore radius frequently depends upon the use of the Kelvin equation. To lend validity to its use in the micropore region, the area under the distribution curve was normalized to  $P_A$ , where A refers to the solvent (11). Then  $P_{Aj}$  is the area of the  $j$ th element of the area under the pore volume distribution curve.

Combining equations (2), (3), and (4), equation 5 is obtained

$$\frac{c_i}{c_f} = 1 - (W/V_A) \left[ P_A - \sum_j \frac{P_{Aj} (r_j - r_B)^2}{(r_j - r_A)^2} \right] \quad (5)$$



where only the pores in which  $r_B > r_i$  are considered. For convenience of calculation, equation (5) can be rearranged to

$$\frac{c_i}{c_f} = 1 - (W/V_A) (P_A - Q_1 r_B^2 + Q_2 r_B - Q_3) \quad , \quad (6)$$

where  $Q_1 = \sum_j Q_j$ ,  $Q_2 = \sum_j 2r_j Q_j$ ,  $Q_3 = \sum_j r_j^2 Q_j$ , and  $Q_j = P_{Aj}/(r_j - r_A)^2$

The  $Q$  coefficients of equation (6) were calculated for each solid from the pore volume distributions for both  $r_A = 1.7 \text{ \AA}$  and  $2.0 \text{ \AA}$ . For water the value of  $r_A = 1.7 \text{ \AA}$  is a lower limit, since for  $\text{Cs}^+$ , which sees the same volume as water (8), the crystal radius is  $1.69 \text{ \AA}$ . The arbitrary choice of  $r_A = 2.0 \text{ \AA}$  is based on the assumption that  $\text{Cs}^+$  is slightly hydrated.

### Experimental

The following procedure was used in a typical experiment (8);  $V$  ml. of solution having a concentration of  $c_i$ , was mixed with  $W$  g. of silica gel. After equilibrium was obtained (usually 48 hours), the external solution was analyzed to obtain  $c_f$ . This was repeated at several concentrations and  $c_i/c_f$  was extrapolated to infinite dilution to avoid concentration effects.

The distribution of pore volume with pore radius was determined by the method of Cranston and Inkley (17) from the nitrogen adsorption isotherm at liquid nitrogen temperature. The isotherms were determined with a sorptometer, which uses the gas chromatography principle (18). The BET surface areas (19), were determined using the sorptometer.

### Results and Discussion

The ion species whose "size" is measured by the use of the geometric effect is the kinetic entity which collides with the uncharged gel surface and is thereby stripped of some of its water of solvation. Solvate radii,  $r_B$  values, are given for three gels in Table I. The value of  $2.0 \text{ \AA}$  for  $r_A$  is chosen;  $r_B$  is slightly different if the value of  $1.7 \text{ \AA}$  is chosen. Although  $c_i/c_f$  is measured for an electrolyte, the  $r_B$  value usually can be assigned to one of the ions. Thus, since  $c_i/c_f = 1$  for  $\text{CsNO}_3$ , the value for any other nitrate (always less than unity) can be used to determine cation size; similarly, with other cesium salts anion size can be determined.

In general, for the  $r_B$  values given it is concluded that (1) the values for different ions on a given gel have a logical relationship to one another, i.e., the ions generally thought to hydrate more are indeed those with the larger  $r_B$  values, (2) the values for a given ion on different gels are in poor agreement, and (3) the values are within the range found using other methods. The geometric effect method of determining size may not be as accurate as some other

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BY JAMES M. SMITH, LL.D.

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methods. However, all methods of determining size are of interest because each method defines uniquely the nature of the quantity being measured. No present method gives information about the size of the solvate when it is in the vicinity of a wall. Another advantage of the exclusion method is that it can be used under rather unusual conditions, e.g., in concentrated acid solutions, and over a wide temperature range.

The following information was obtained from the records of the Department of the Interior, Bureau of Land Management, for the year ending December 31, 1964.

The total number of acres of land owned by the United States is 1,040,000,000. The total number of acres of land owned by the States is 1,040,000,000. The total number of acres of land owned by the Federal Government is 1,040,000,000.

Table I. Summary of Ion Solvate Radii

| Ion                           | $r_B$ , Å            |                             |                             | Radii |
|-------------------------------|----------------------|-----------------------------|-----------------------------|-------|
|                               | Code 70 <sup>a</sup> | Code 40, W. W. <sup>b</sup> | Code 40, A. W. <sup>c</sup> |       |
| H <sup>+</sup>                | ---                  | 4.0                         | 5.0                         | 2.82  |
| Li <sup>+</sup>               | 5.1                  | 4.1                         | 6.7                         | 3.82  |
| Na <sup>+</sup>               | 4.8                  | 4.0                         | ---                         | 3.58  |
| K <sup>+</sup>                | 3.4                  | 3.3                         | 5.0                         | 3.31  |
| Rb <sup>+</sup>               | ---                  | 2.6                         | ---                         | 3.29  |
| Cs <sup>+</sup>               | ---                  | (2.0)                       | ---                         | 3.29  |
| Be <sup>++</sup>              | ---                  | 5.4                         | ---                         | 4.59  |
| Mg <sup>++</sup>              | 5.4                  | 4.3                         | ---                         | 4.28  |
| Ca <sup>++</sup>              | ---                  | 4.2                         | ---                         | 4.12  |
| Sr <sup>++</sup>              | 5.8                  | 4.1                         | ---                         | 4.12  |
| Ba <sup>++</sup>              | ---                  | 4.4                         | ---                         | 4.04  |
| Al <sup>+++</sup>             | 7.0                  | 5.0                         | 6.3                         | 4.75  |
| In <sup>+++</sup>             | ---                  | 5.3                         | ---                         | ---   |
| Cr <sup>+++</sup>             | 5.7                  | 5.3                         | 6.4                         | 4.61  |
| Mn <sup>++</sup>              | ---                  | 4.1                         | ---                         | 4.38  |
| Fe <sup>+++</sup>             | ---                  | ---                         | 7.3                         | 4.28  |
| Co <sup>++</sup>              | 5.6                  | 4.8                         | ---                         | 4.23  |
| Ni <sup>++</sup>              | ---                  | 4.6                         | 6.8                         | 4.04  |
| Cu <sup>++</sup>              | ---                  | 4.3                         | 4.9                         | 4.19  |
| Y <sup>+++</sup>              | ---                  | ---                         | 5.9                         | ---   |
| Ag <sup>+</sup>               | ---                  | 3.8                         | ---                         | 3.41  |
| La <sup>+++</sup>             | ---                  | ---                         | 5.9                         | ---   |
| Ge <sup>+++</sup>             | ---                  | ---                         | 5.8                         | ---   |
| Pr <sup>+++</sup>             | ---                  | ---                         | 5.8                         | ---   |
| Nd <sup>+++</sup>             | ---                  | ---                         | 5.5                         | ---   |
| Sm <sup>+++</sup>             | ---                  | ---                         | 6.0                         | ---   |
| Gd <sup>+++</sup>             | ---                  | ---                         | 5.6                         | ---   |
| Th <sup>+4</sup>              | ---                  | ---                         | 6.6                         | ---   |
| UO <sub>2</sub> <sup>++</sup> | ---                  | 4.1                         | 6.3                         | ---   |
| Cl <sup>-</sup>               | ---                  | ---                         | 2.7                         | 2.10  |
| Br <sup>-</sup>               | ---                  | ---                         | 3.4                         | 3.30  |
| I <sup>-</sup>                | ---                  | ---                         | 3.8                         | 3.30  |

a.  $P_A = 1.15$  ml/g; Surface area = 352 m<sup>2</sup>/g.

b.  $P_A = 0.40$  ml/g; Surface area = 594 m<sup>2</sup>/g.

c.  $P_A = 0.40$  ml/g; Surface area = 498 m<sup>2</sup>/g.



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# HYDRIDO COMPLEXES OF TRANSITION METALS

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August 4, 1964

## INTRODUCTION

It has been long recognized that all elements, except the transition metals(1,2), form hydrides in which the hydrogen can form a bond with the metal atoms. These hydrides have been classified as those formed by electropositive elements and are said to be ionic, e.g., NaH, KH; and those formed by electronegative elements and are said to be covalent and volatile, e.g., H<sub>2</sub>O, H<sub>2</sub>S. The salt-like hydrides(2), e.g., AlH<sub>3</sub> are considered to be between these two types. Up to 1952, no molecular transition-metal hydrides were known except [FeH<sub>2</sub>(CO)<sub>4</sub>] and [CoH(CO)<sub>4</sub>](1,2) which are volatile but very unstable, decomposing even at -20°C, and which behave as weak acids in water. The situation before 1952 is illustrated in Fig. 1 from which it will be seen that the main gap in the hydride chemistry falls among the transition elements.

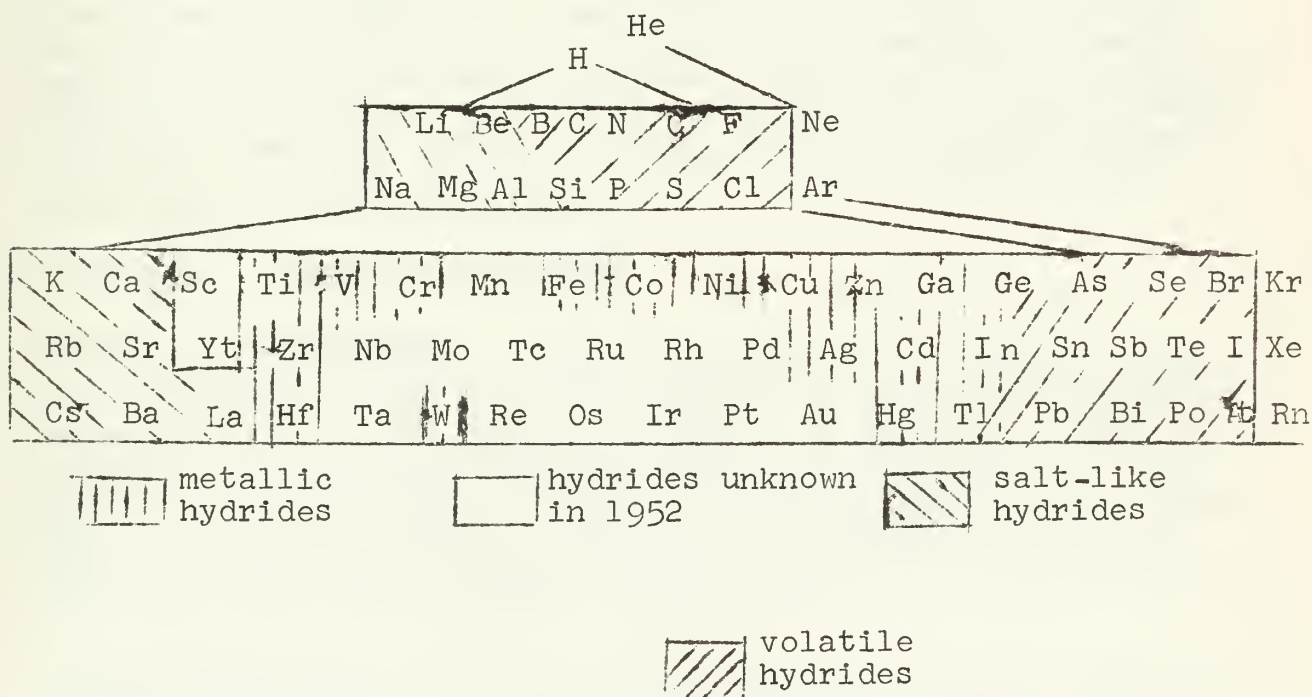


Figure 1. Elements were known in 1952 to form simple hydrides

However, in 1955, [ReH(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>](3,4,5) was discovered by accident during the attempted preparation of biscyclopentadienylrhodium. This discovery was followed in 1957, by the discovery of transition-metal hydrides which were stabilized by tertiary phosphines (1,2) e.g., trans-[Pt(H)Cl(PEt<sub>3</sub>)<sub>2</sub>] and which were stable enough to



allow complete study of the nature and properties of the coordinated hydride ion. In 1960, a new type of hydrido complex stabilized by tertiary phosphines or tertiary arsines, and carbon monoxide, e.g.,  $[\text{Ir}(\text{H})\text{Cl}_2(\text{CO})(\text{Ph}_3\text{P})_2](23)$  or  $[\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PEt}_2\text{Ph})_3](25)$  was discovered; this type was considered to be the more stable.

The scope of this seminar will be limited to a discussion of the bonding and properties of the hydrogen in these complexes with brief reference to the preparative methods.

The general formula of the hydrido-complexes of transition metals can be either  $[\text{M}^{\text{m}}\text{H}^{\text{n}}\text{L}^{\text{p}}](1)$  or  $[\text{MH}^{\text{x}}\text{X}^{\text{y}}\text{L}^{\text{z}}]_n(2)$ , where M is a transition metal atom; L is an effective ligand of high-field strength (other than hydrogen) which can stabilize the metal-to-hydrogen bond, e.g., CO, NO, CN, tertiary phosphine, and cyclopentadienyl ion; n is usually equal to one or sometimes equal to two as in  $[\text{FeH}_2(\text{CO})_4]$ ; and x is a univalent anionic ligand as halide ion. The complexes having these formulas are usually nonelectrolytes(1,2,6,8) and diamagnetic (i.e., the metal d-electrons are paired under the influence of the high-field strength of the ligand L). The metal atom in these complexes usually has the effective atomic number of the next inert gas. The metal-to-hydrogen bond is shorter than the radius sum(9,10) because of the very close association of the hydrogen to the metal which appears to be bonded directly to it. Some of these complexes behave as acids(9,11), e.g., those derived from group VI metals; and some behave as bases(11), e.g.,  $[\text{ReH}(\text{C}_5\text{H}_5)_2]$ ,  $[\text{MoH}_2(\text{C}_5\text{H}_5)_2]$ , and  $[\text{WH}_2(\text{C}_5\text{H}_5)_2]$ .

## PROPERTIES OF HYDRIDO COMPLEXES

### Ligand-field Strength:

The hydrido ligand in these complexes has a large ligand-field strength. That is, the bands due to  $d \rightarrow d$  transitions are shifted to the ultraviolet region. An example to that is in trans- $[\text{RuCl}_2(\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2]$  the  $d \rightarrow d$  transition occurs at 411 m $\mu$ , but in trans- $[\text{Ru}(\text{H})\text{Cl}(\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2]$  this transition occurs below 364 m $\mu$ . This is why the hydride ion was classified with those groups, such as methyl and cyanide ion, that have high-ligand field strength(13).

### Thermal Stability:

It is known that the highest element in a group forms the most stable hydride(1,9,12). This is found to be true in a series of compounds of the type  $[\text{MHC}_5\text{H}_5(\text{CO})_3]$  where M = Cr, Mo, and W, but that is not true for the carbonyl hydrides(12) where  $[\text{MnH}(\text{CO})_5]$  is more stable than  $[\text{ReH}(\text{CO})_5]$ . However, the order of stability(1,2) of these compounds lies in the sequence: carbonyl hydrides < cyclopentadienyl hydrides < cyclopentadienyl carbonyl hydrides < tertiary phosphine hydrides. These facts are observed for the nickel group of compounds, which have the





formula  $[M(H)Cl(PEt_3)_2]$ ; the platinum compound(12) is very stable and can be easily isolated, but the corresponding nickel compound has never been isolated. Another example is given in table I.

Table I

Thermal stability of compounds of the type  
 $[M(H)Cl(Et_2PCH_2CH_2PEt_2)_2]$

| <u>M</u> | <u>Decomposition point, °C</u> | <u>Melting point, °C</u> |
|----------|--------------------------------|--------------------------|
| Fe       | 155                            | 155                      |
| Ru       | 310                            | 175                      |
| Os       | 315                            | 171                      |

Nuclear magnetic resonance spectra:

The hydride ion in these complexes has a very large chemical shift(9,14,15) towards high fields as shown by NMR spectra (table II).

This large shift might indicate high electron density at the proton. Also it can be explained by the large shielding effects caused by the field generated by a paramagnetic electron circulation which is induced by the applied magnetic field in the non-bonding d-electrons at the metal atom. However, this large shift cannot primarily be attributed to S electrons(9) of the hydrogen.

Table II

Proton chemical shift in p.p.m. of the hydride ion in some hydrido complexes relative to benzene

| <u>Compound</u>            | <u>Chemical shift</u> | <u>Reference</u> |
|----------------------------|-----------------------|------------------|
| $trans-[Pt(H)Cl(PEt_3)_2]$ | 22.4                  | 2                |
| $trans-[Pt(H)Br(PEt_3)_2]$ | 20.9                  | 2                |
| $trans-[Pt(H)I(PEt_3)_2]$  | 18.0                  | 2                |
| $[CrH(C_5H_5)(CO)_3]$      | 13.1                  | 9                |
| $[MoH(C_5H_5)(CO)_3]$      | 12.8                  | 9                |
| $[WH(C_5H_5)(CO)_3]$       | 14.7                  | 9                |
| $[ReH(C_5H_5)_2]$          | 20.5                  | 9                |
| $[FeH_2(CO)_4]$            | 17.4                  | 9                |
| $[CoH(CO)_4]$              | 17.3                  | 9                |

This large shift for the hydride ion is considered to be well separated(14) from that due to the protons in the organic part of the molecule as shown by the following spectra in Figures 2 and 3 for the compounds  $[Pt(H)Cl(PEt_3)_2]$ (2) and  $[Ru(H)I(chelate)_2]$ (14), respectively, where chelate is  $C_2H_4(PMe_2)_2$ ,  $C_2H_4(PEt_2)_2$ , or  $o-C_6H_4(AsMe_2)_2$ .





Figure 2. NMR spectrum of  $\text{trans-[Pt(H)Cl(PEt}_3)_2]$  in  $\text{CCl}_4$ .



Figure 3. NMR spectrum of  $\text{trans-[Ru(H)I(PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2]$  in  $\text{CH}_3\text{Cl}$ .

The low-field line in Fig. 2 represents the chemical shift of the organic ligand protons, and the high-field line represents the chemical shift of the hydrogen attached to the metal atom. The high-field line is split into a triplet by the two equivalent phosphorous nuclei ( $\text{spin} = 1/2$ ). In Fig. 3, the high-field resonance line is split into five sharp, equally spaced lines (intensity ratio 1:4:6:4:1) by the coupling of the four equivalent phosphorous nuclei of the chelate groups with the hydrogen nucleus.

#### Infrared spectra:

Infrared spectra of these compounds has a strong absorption band(16,17,18) characteristic of the metal-to-hydrogen stretching frequency in the region  $1700\text{-}2000\text{ cm}^{-1}$ , and another band characteristic of the metal-to-hydrogen bending vibration in the region  $600\text{-}900\text{ cm}^{-1}$ . The metal-to-hydrogen stretching frequencies for a number of hydride compounds are shown in table III.

Table III

Stretching frequencies in  $\text{cm}^{-1}$  of the metal-to-hydrogen bond for some hydrido complexes

| <u>Compound</u>   | <u><math>\nu_{\text{M-H}}</math></u> | <u>Reference</u> |
|---|--------------------------------------|------------------|
| $[(\text{C}_5\text{H}_5)_2\text{MoH}_2]$                            | 1847                                 | 11               |
| $[(\text{C}_5\text{H}_5)_2\text{WH}_2]$                             | 1896                                 | 11               |
| $[(\text{C}_5\text{H}_5)_2\text{TaH}_3]$                            | 1735                                 | 11               |
| $\text{trans-[FeH}_2\{\text{o-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$  | 1726                                 | 2                |
| $[\text{M(H)Cl}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2]$ |                                      |                  |
| M = Fe  | 1849                                 | 1                |
| = Ru  | 1938                                 | 1                |
| = Os  | 2039                                 | 1                |



The hydrogen in these compounds is sensitive to its environments(2) and, consequently, the stretching frequency of M-H bond will be affected by other ligands attached to the metal atom. This situation for platinum complexes(19,20) of the formula  $[(ER_3)_2Pt(H)X]$  is illustrated in table IV.

Table IV

The effect of various anionic ligands on the metal-to-hydrogen stretching frequency,  $cm^{-1}$ , for compounds of the type  $[(ER_3)_2Pt(H)X]$

| <u>ER<sub>3</sub></u> | <u>NO<sub>3</sub></u> | <u>Cl</u> | <u>Br</u> | <u>I</u> | <u>NO<sub>2</sub></u> | <u>SCN</u> | <u>CN</u> |
|-----------------------|-----------------------|-----------|-----------|----------|-----------------------|------------|-----------|
| PMe <sub>3</sub>      |                       | 2182      |           |          |                       |            |           |
| PEt <sub>3</sub>      | 2242                  | 2183      | 2178      | 2156     | 2150                  | 2112       | 2041      |
| PPhEt <sub>2</sub>    |                       | 2199      |           | 2179     |                       |            |           |
| ASet <sub>3</sub>     |                       | 2174      | 2167      | 2139     |                       | 2108       |           |

The anionic ligands in table IV are placed in the order of increasing trans-effect and also in the order of decreasing metal-to-hydrogen stretching frequencies and decreasing metal-to-hydrogen bond strength. It can be seen that the stretching frequency of the metal-to-hydrogen decreases in passing from chlorine to iodine; this can be explained by the fact that iodine, by the mesomeric effect which is caused by platinum II ion, attracts the electrons more than the chlorine does and hence the M-H stretch is decreased with iodine. This effect, (table V), is completely different(18) for the compounds of the type  $[M(H)X(diphos)_2]$  where M = Fe, Ru, or Os; X = halide ion; and diphos =  $PEt_2CH_2CH_2PEt_2$ .

Table V

The effect of halide ions on the metal-to-hydrogen stretching frequency for the compounds indicated

| <u>Compound</u>      | x = <u>Cl</u>  | <u>I</u>       |
|----------------------|----------------|----------------|
| $[Fe(H)X(diphos)_2]$ | 1849 $cm^{-1}$ | 1872 $cm^{-1}$ |
| $[Ru(H)X(diphos)_2]$ | 1938           | 1948           |
| $[Os(H)X(diphos)_2]$ | 2039           | 2051           |

The effect in compounds of table V is mostly an inductive effect by which the chlorine is more effective than iodine in attracting the electrons and hence the M-H stretching frequency is decreased with chlorine. The order of decreasing the M-H stretching frequencies for the iridium compounds (6,7,8) of the type  $[Ir(H)Cl_2(ER_3)_3]$  where  $ER_3$  is  $Ph_3P$ ,  $Ph_3As$ , or  $Ph_3Sb$  lies in the sequence:  $(Ph_3P)_3 > (Ph_3As)_3 > (Ph_3Sb)_3$ .

The metal-to-hydrogen stretching frequency was also found to be susceptible to the nature of the solvents in which the spectra





are measured (2,16). Higher frequency was reported with polar solvents. Table VI shows the  $\Delta\nu_{M-H}$  values (where  $\Delta\nu_{M-H} = \nu_{M-H} \text{ chloroform} - \nu_{M-H} \text{ hexane}$ ) for the compounds indicated.

Table VI

Effect of the solvent on the M-H stretching frequencies.

| Compound  | $\nu_{M-H} \text{ hexane}$ | $\Delta\nu_{M-H}$   |
|---|----------------------------|---------------------|
| I <u>trans</u> -[Pt(H)Cl(PEt <sub>3</sub> ) <sub>2</sub> ]                | 2185 cm <sup>-1</sup>      | 30 cm <sup>-1</sup> |
| II <u>trans</u> -[Ir(H)Cl <sub>2</sub> (PEt <sub>3</sub> ) <sub>3</sub> ] | 2090                       | 7                   |
| III <u>Cis</u> -[Ir(H)Cl <sub>2</sub> (PEt <sub>3</sub> ) <sub>3</sub> ]  | insoluble                  | 35                  |
| IVa [IrH <sub>2</sub> Cl(PEt <sub>2</sub> Ph) <sub>3</sub> ]*             | 2162                       | 34                  |
| IVb [IrH <sub>2</sub> Cl(PEt <sub>2</sub> Ph) <sub>3</sub> ]**            | 2026                       | 0                   |
| V <u>trans</u> -[IrHCl <sub>2</sub> (AsEt <sub>3</sub> ) <sub>3</sub> ]   | 2099                       | 0                   |

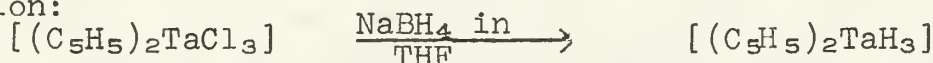
\*Hydrogen atom is trans- to chlorine

\*\*Hydrogen atom is trans to a trisubstituted phosphine.

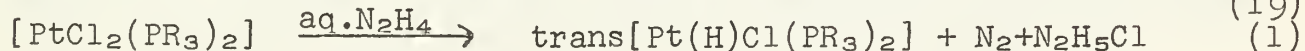
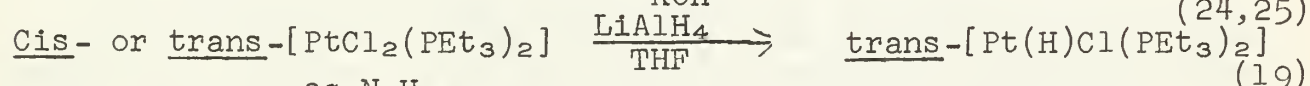
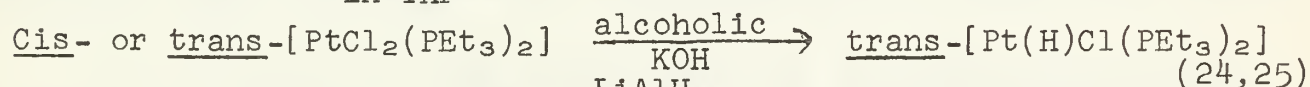
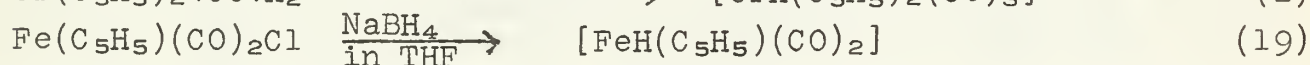
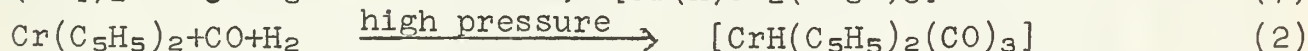
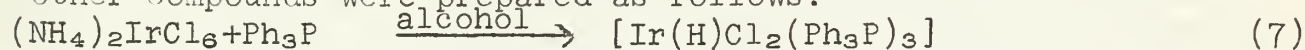
These values indicate that  $\Delta\nu_{M-H}$  is large when the hydrogen is trans to chlorine; the hydrogen in this case is solvent sensitive, but solvent insensitive when it is trans to a trisubstituted phosphorous or arsine (IVb and V in table VI).

## PREPARATION

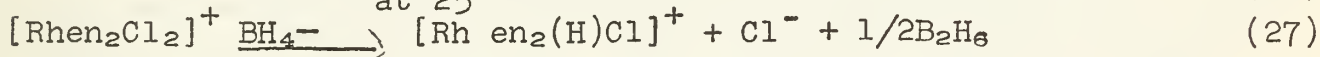
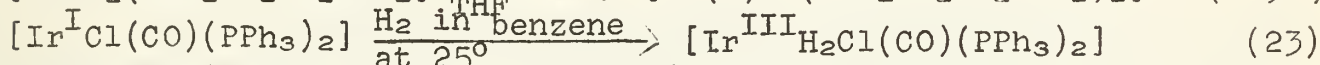
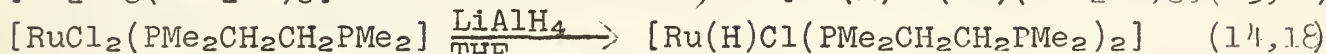
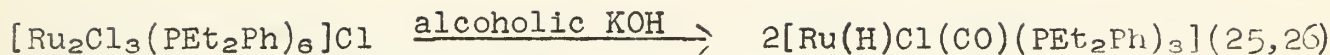
In general, these compounds are prepared(11,22,24) by the interaction of the anhydrous halides with a solution of the desired ligand in a suitable solvent, or by the reduction(17,18) of the corresponding halogeno-complexes by some reducing agents in solvent media. It is believed that the solvent acts as a proton-transfer agent. Various reducing agents and solvent media have been used, including lithium aluminium hydride in tetrahydrofuran, alcoholic potassium hydroxide, alcoholic hypophosphorous acid, aqueous hydrazine, and even molecular hydrogen(23,28) in benzene. Compounds(15) of the type [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MH<sub>X</sub>] were prepared according to the following equation:



Other compounds were prepared as follows:







## BONDING AND STRUCTURE

The most significant information about the structure and bonding of these compounds comes from the high-resolution nuclear magnetic resonance studies on the compound  $[(\text{C}_5\text{H}_5)_2\text{TaH}_3]$  (15) whose spectrum was reported to contain: A resonance line (relative intensity = 10) at  $T = 5.25$ , assigned to the ten equivalent protons in the two  $\text{C}_5\text{H}_5$  groups; a triplet (relative intensity = 1) at  $T = 11.63$ ; and a doublet (relative intensity = 2) at  $T = 13.08$ . The triplet and the doublet resonance lines that occur on the high-field side relative to tetramethylsilane indicate the presence of three protons attached to the metal atom (4,29); two protons are in equivalent environments, while the third is different. Hence, it is considered that all of the compounds  $[(\text{C}_5\text{H}_5)_2\text{MH}_x]$  have three orbitals that are not involved in the metal-to-ring bonding (11,22), two orbitals are equivalent, these are the A-labeled orbitals in Figure 4.

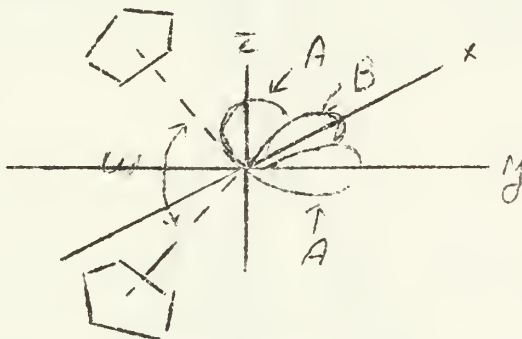


Figure 4. The bonding scheme of the compound  $[(\text{C}_5\text{H}_5)_2\text{TaH}_3]$ .

All three orbitals are available for bonding to hydrogen or for occupation by lone pairs of electrons. In the compound  $[(\text{C}_5\text{H}_5)_2\text{TaH}_3]$ , all these orbitals are involved in bonding to the hydrogens, but in the compound  $[\text{ReH}(\text{C}_5\text{H}_5)_2]$  only one orbital is used by hydrogen and in the compounds  $[(\text{C}_5\text{H}_5)_2\text{MoH}_2]$ ,  $[(\text{C}_5\text{H}_5)_2\text{WH}_2]$ , and  $[(\text{C}_5\text{H}_5)_2\text{ReH}_2]^+$  two orbitals are used; the remaining orbitals are filled by lone pairs of electrons. These facts explain why the compound  $[(\text{C}_5\text{H}_5)_2\text{ReH}]$  and possibly  $[(\text{C}_5\text{H}_5)_2\text{MoH}_2]$ ,  $[(\text{C}_5\text{H}_5)_2\text{WH}_2]$  behave as bases, while the compounds  $[(\text{C}_5\text{H}_5)_2\text{TaH}_3]$  and  $[(\text{C}_5\text{H}_5)_2\text{WH}_3]^+$  do not show any basic behavior.

The two metal-to-ring axes (31,10) are believed to be at an angle  $\underline{W}$  to each other, (Fig. 4) except the neutral ferrocene-like compounds. However, x-ray structure determination indicated this angular situation (30) for the cyclopentadienyl rings in the compound  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2\text{Al}(\text{C}_2\text{H}_5)_2$ . This was also said (10,15) to be possible in the range  $135^\circ \leq W \leq 80^\circ$  since there is a little loss in the metal-to-ring bonding energy and consequently this binding







energy becomes not very dependent on whether the rings axes are collinear or angular.

The non-linearity of the rings was confirmed(10) by the single crystal x-ray analysis of the compound  $[(C_5H_5)_2MoH_2]$  which shows that this molecule is "wedge-like" as in Fig. 5, and the angle between the rings is  $25^\circ \pm 3^\circ$ . The bond angle H-Mo-H is  $90^\circ \pm 10^\circ$ , and the estimated Mo-H bond distance ( $1.1 \pm 0.2 \text{ \AA}$ ) is less than the radius sum which indicates that the hydrogen in these compounds is bound directly to the non-bonding d-electrons of the metal atom(9).

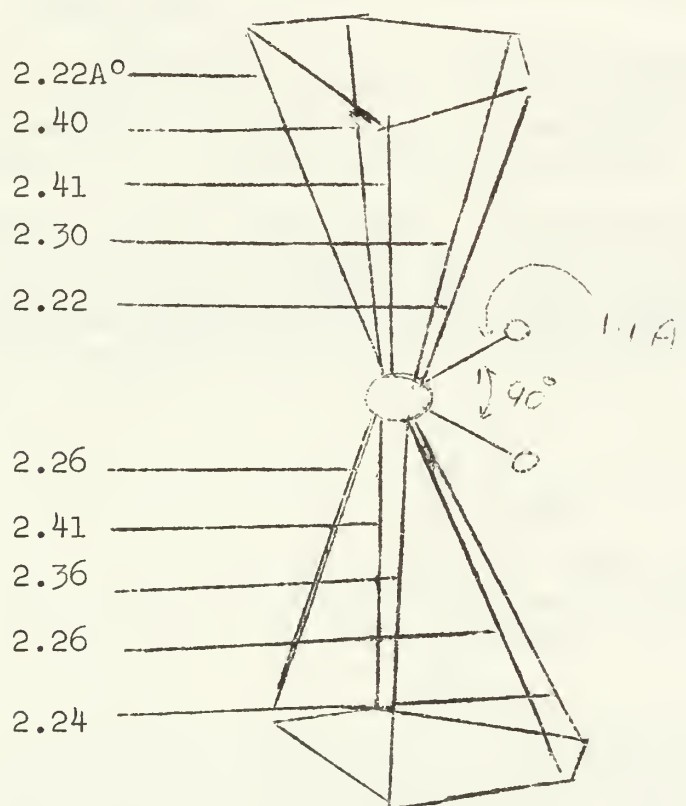


Figure 5. Structure of the molecule  $[(C_5H_5)_2MoH_2]$

On the basis of the last argument, the hydrogen might be located between the ring and the metal atom(1,4). This gives three possible types of structure to the compound  $[ReH(C_5H_5)_2]$  and also to its cation  $[ReH_2(C_5H_5)_2]^+$  as shown in Fig. 6.



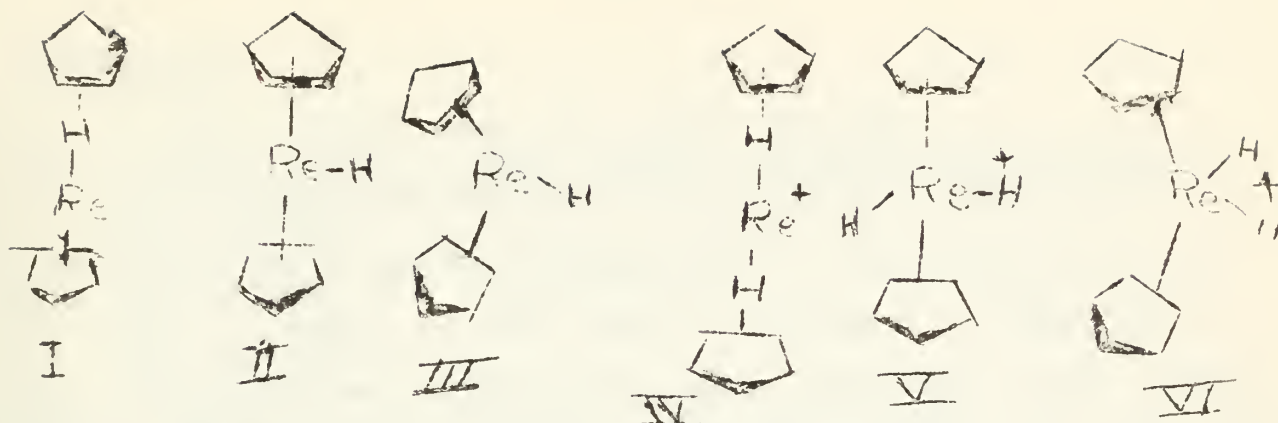


Figure 6. Structures of the compounds  $[\text{ReH}(\text{C}_5\text{H}_5)_2]$  and  $[\text{ReH}_2(\text{C}_5\text{H}_5)_2]^+$

Structure I is considered to be unlikely because the two rings are not in the same environments. In structure II, the rings are aligned and in III are likely to represent the molecule since the two rings are in equivalent environments.

Compounds of the type trans -  $[\text{Pt}(\text{H})\text{X}(\text{PR}_3)_2](2)$ , (where x is halide), in which the hydrogen was proved to be present as an anionic ligand, have been shown by x-ray structure determination to have a planar structure for the heavy ligands and the hydrogen was shown to complete the square coordination, Fig. 7.

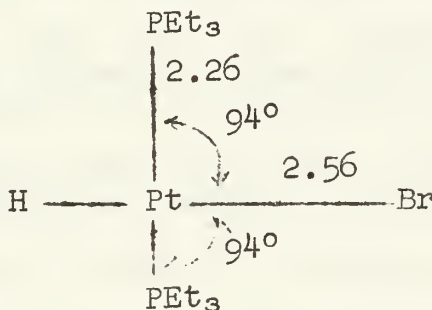


Figure 7. Structure of the compound  $[\text{Pt}(\text{H})\text{Br}(\text{PEt}_3)_2]$

The Pt-P bond distance is less than the radius sum because of the partial double bond character, while the Pt-Br bond distance is greater than the radius sum because of the ionic character and the polarity of this bond caused by the presence of the hydride ion which is in the position trans to the bromine.

## CONCLUSION

It can be concluded that the hydrido complexes have now been established for a large number of transition metals, and hydrogen atoms attached to transition metals can be easily detected by the nuclear magnetic resonance technique which makes the metal-to-hydrogen bond more familiar and common than was previously thought. One of the characteristics of these compounds is the high-field shift observed for the protons by this technique.



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# SOME ORGANOMETALLIC CHEMISTRY OF GROUP IIB

Larry M. Seitz

November 17, 1964

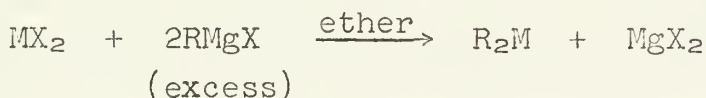
## Introduction

Diethylzinc and ethylzinc iodide, first prepared by Frankland in 1849 (1), were the first truly organometallic compounds reported. Actually the simple organozinc compounds have a notable place in the history of chemistry, since studies on their vapor densities and chemical reactions led Frankland to postulate the first clear valence theory in which he suggested each element had a definite limited combining capacity (2). Frankland used diethylzinc so widely to make other organometallic compounds that he may properly be called the founder of the chemistry of organometallic compounds (3).

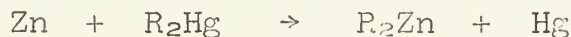
Frankland's original method for the preparation of dialkylzinc compounds involves the thermal decomposition of alkylzinc iodides, the latter being prepared by direct reaction of alkyl halides with a zinc-copper alloy. The alkylzinc compounds are distilled from the reaction mixture. Improvements include the use of a special zinc-copper alloy and high boiling ethers as solvents (4).

Coates (4) has compiled a wealth of information concerning the preparations of the organometallic compounds of this group and this reference provides a good source to the early literature. Some of the more common general methods are summarized below.

The dialkyls or diaryls of this group can be obtained by the reaction of the anhydrous metal halides with a Grignard solution.



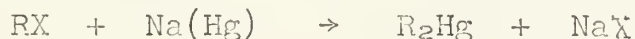
The more volatile dialkyls may be distilled from the reaction mixture. Organozinc compounds can be prepared by heating zinc metal with the appropriate organomercury compound. However, with



cadmium an equilibrium results. The diaryls of zinc and cadmium



can be obtained by the reaction of the metal halides with aryl-lithium reagents in ether. Both dialkyls and diaryls of mercury can be prepared from sodium amalgam and the appropriate halide diluted with xylene.







The dialkyl compounds of this group are all volatile liquids, e.g., the boiling points for  $\text{Me}_2\text{Zn}$ ,  $\text{Me}_2\text{Cd}$ , and  $\text{Me}_2\text{Hg}$  are  $44^\circ$ ,  $105.5$ , and  $92^\circ\text{C}$ , respectively. The diaryls are all solids. Sensitivity to air varies considerably with dimethylzinc being spontaneously inflammable in air, dimethylcadmium only inflammable when a large surface area is exposed, and finally dimethylmercury does not react at all with oxygen or water under normal conditions. On the other hand, the thermal stability of the dialkyls decreases in the order  $\text{R}_2\text{Zn} > \text{R}_2\text{Cd} > \text{R}_2\text{Hg}$ .

### Structure and Bonding

The dialkyls and diaryls of this group are monomeric and have linear structures. Infrared and Raman spectra of  $\text{Me}_2\text{Hg}$  and  $\text{Me}_2\text{Zn}$  support a linear C-M-C structure with essentially free rotation of the methyl groups (5). Also an X-ray structure study of  $\text{Me}_2\text{Zn}$  by Rundle (6) shows that the crystal consists of linear monomers. Linear structures, of course, are in agreement with the metal atoms using sp orbitals in bonding to the organo-groups.

At this point, however, it is necessary to note that mercury has a special tendency to form compounds in which the metal is attached to only two ligands. Orgel (7) has attributed this to d-s mixing rather than to the special stability of sp-hybrid bonds. As the data in Table I indicates, the s-p separation in Hg is slightly greater than in Zn or Cd, but it is thought it is not large enough to account for the large extra stability of the linear structure. On the other hand, the energy of the lowest  $d^9s$  state above the  $d^{10}$  ground state for mercury is only about one half the value for cadmium or zinc, and is even less than the s-p separations. Although some sp hybridization cannot be completely excluded, it must also be supposed that mercury uses a combination of one 6p orbital and one d-s orbital (mixing of the 5dz orbital with the 6s orbital) in its bonding to the organo-groups.

Table I

|    | Energy ( $\text{cm}^{-1}$ ) of lowest $d^9s$ state<br>above the $d^{10}$ ground state ( $\text{M}^{++}$ ions) | E (s-p) of $\text{M}^+$ ( $\text{cm}^{-1}$ ) |
|----|---|--|
| Zn | 78,105  | 49,000                                       |
| Cd | 80,463  | 45,800                                       |
| Hg | 42,862  | 57,600                                       |



## Coordination Complexes

An indication of the existence of coordination complexes was the observation made in 1859 by Frankland (8) that the use of dimethyl or diethyl ether as a solvent greatly facilitates the formation of dimethylzinc from zinc and methyl iodide, and that separation from the solvent proved to be impossible. However, no one seemed to pay much attention to this, and in fact even for many years it was generally thought that organozinc or organocadmium compounds were unable to form neutral donor-acceptor complexes. Recently examples of coordination complexes have been reported and most of these are listed in Tables II and III.

Table II  
Coordination Complexes of  $\text{Me}_2\text{Zn}$  and  $\text{Me}_2\text{Cd}$

| <u>Complex</u>  | <u>M.P.<br/>°C</u> | <u>B.P.<br/>°C</u> | <u>Ref.<br/>No.</u> | <u>Remarks</u>                          |
|---|--------------------|--------------------|---------------------|---|
| $\text{Me}_2\text{Zn} \cdot \text{NMe}_3$                 | -52                | 84                 | 28                  |   |
| $\text{Me}_2\text{Zn} \cdot 2\text{NMe}_3$                | 84                 | -                  | 28                  |   |
| $\text{Me}_2\text{Zn} \cdot \text{NEt}_3$                 | 95                 | -                  | 28                  | Dissociates in benzene                  |
| $\text{Me}_2\text{Zn} \cdot \text{C}_5\text{H}_5\text{N}$ | 44                 | -                  | 28                  | " " "                                   |
| $\text{Me}_2\text{Zn} \cdot \text{TEED}^a$                | 66                 | -                  | 28                  | Does not dissociate in benzene          |
| $\text{Me}_2\text{Cd} \cdot \text{TMED}^b$                | 80                 | -                  | 11                  | Dissociates readily                     |
| $\text{Me}_2\text{Zn} \cdot \text{Bipy}^c$                | -                  | -                  | 28                  | Can be vacuum distilled                 |
| $\text{Me}_2\text{Cd} \cdot \text{Bipy}$                  | -                  | -                  | 11                  | High dissociation pressure at room temp |
| $\text{Me}_2\text{Zn} \cdot \text{Phenan}^d$              | -                  | -                  | 28                  | Can be vacuum distilled                 |
| $\text{Me}_2\text{Cd} \cdot \text{Phenan}$                | -                  | -                  | 11                  | Decomposes above 85°                    |
| $\text{Me}_2\text{Zn} \cdot \text{OMe}_2$                 | -                  | 46                 | 12                  | Distills without decomposition          |
| $\text{Me}_2\text{Zn} \cdot \text{O}(\text{CH}_2)_2$      | -                  | 47                 | 12                  | Distillable at atmospheric pressure     |
| $\text{Me}_2\text{Zn} \cdot \text{O}(\text{CH}_2)_3$      | -2.5               | -                  | 12                  | Distillable at atmospheric pressure     |
| $\text{Me}_2\text{Zn} \cdot 1.2 \text{ O}(\text{CH}_2)_3$ | -                  | 80                 | 12                  | This composition distills at 80°        |
| $\text{Me}_2\text{Zn} \cdot 2 \text{ C}(\text{CH}_3)_4$   | -                  | 83                 | 12                  | Distillable at atmospheric pressure     |



Table II (continued)

| Complex  | M.P.<br>°C | B.P.<br>°C | Ref.<br>No. | Remarks   |
|--|------------|------------|-------------|---|
| $\text{Me}_2\text{Cd} \cdot \text{O}(\text{CH}_2)_4$   | -          | 105        | 11          | Distills with some decomposition  |
| $\text{Me}_2\text{Zn} \cdot 2 \text{O}(\text{CH}_2)_5$ | -          | 93.5       | 12          | Distillable at atmospheric pressure   |
| $\text{Me}_2\text{Zn} \cdot (1,4\text{-dioxane})$      | 66         | -          | 27          | Distills with decomposition   |
| $\text{Me}_2\text{Cd} \cdot (1,4\text{-dioxane})$      | 57         | -          | 11          | Sublimes at 30° and 5 mm Hg pressure  |
| $\text{Me}_2\text{Zn} \cdot (1,4\text{-thioxane})$     | 23.5       | -          | 27          | Distills with decomposition   |
| $\text{Me}_2\text{Zn} \cdot 2 \text{ diglyme}^e$       | -          | 91         | 27          | Distills without decomposition, but dissociates in non-polar solvents to diglyme and the 1:1 chelate adduct |
| $\text{Me}_2\text{Zn} \cdot \text{diglyme}$            | 5.5        | -          | 27          | Decomp. 75° to $\text{Me}_2\text{Zn} + 1:2$ adduct  |

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<sup>a</sup> TEED = N,N,N',N'-tetraethylethylenediamine

<sup>b</sup> TMED = N,N,N',N'-tetramethylethylenediamine

<sup>c</sup> Bipy = 2,2'-bipyridine

<sup>d</sup> Phenan = 1,10-phenanthroline

<sup>e</sup> diglyme = ethyleneglycol dimethyl ether





Table III

Some Coordination Complexes of Other  
Organozinc Compounds (10)

| <u>Complex</u>  | <u>R</u>   | <u>M.P.</u>                |
|---|--|----------------------------|
| $  \begin{array}{c}  \text{H}_2\text{C} - \text{CH}_2 \\    \quad   \\  \text{CH}_3 - \text{O} \quad \text{O} - \text{CH}_3 \\  \diagdown \quad \diagup \\  \text{Zn} \\  \diagup \quad \diagdown \\  \text{R} \quad \text{R}  \end{array}  $                                       | $\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$                           | 60-61<br>108-109           |
| $  \begin{array}{c}  \text{H}_2\text{C} - \text{CH}_2 \\    \quad   \\  \text{Me} \quad \text{N} \quad \text{N} \quad \text{Me} \\    \quad   \quad   \quad   \\  \text{Me} \quad \text{Zn} \quad \text{Me} \\  \diagdown \quad \diagup \\  \text{R} \quad \text{R}  \end{array}  $ | $\text{C}_4\text{H}_9$<br>$\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$ | liq.<br>123-124<br>161-162 |
| $  \begin{array}{c}  \text{N} - \text{N} \\    \quad   \\  \text{Me} \quad \text{N} \quad \text{N} \quad \text{Me} \\    \quad   \quad   \quad   \\  \text{Me} \quad \text{Zn} \quad \text{Me} \\  \diagdown \quad \diagup \\  \text{R} \quad \text{R}  \end{array}  $              | $\text{C}_4\text{H}_9$<br>$\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$ | -45<br>54-55<br>136-137    |
| $  \begin{array}{c}  \text{P}\phi_3 \quad \text{P}\phi_3 \\  \diagdown \quad \diagup \\  \text{Zn} \\  \diagup \quad \diagdown \\  \text{R} \quad \text{R}  \end{array}  $  | $\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$                           | 142-143<br>166-167         |
| $  \begin{array}{c}  \text{H}_2\text{C} - \text{CH}_2 \\    \quad   \\  \phi \quad \text{P} \quad \text{P} \quad \phi \\    \quad   \quad   \quad   \\  \phi \quad \text{Zn} \quad \phi \\  \diagdown \quad \diagup \\  \text{R} \quad \text{R}  \end{array}  $                     | $\text{C}_4\text{H}_9$<br>$\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$ | 114<br>185-187<br>211-213  |
| $  \begin{array}{c}  \text{Me} \quad \text{As} \quad \text{As} \quad \text{Me} \\    \quad   \quad   \quad   \\  \text{Me} \quad \text{Zn} \quad \text{Me} \\  \diagdown \quad \diagup \\  \text{R} \quad \text{R}  \end{array}  $  | $\text{C}_4\text{H}_9$<br>$\text{C}_6\text{H}_5$<br>$\text{C}_6\text{F}_5$ | liq.<br>132-133<br>136-137 |



The stability of the neutral donor-acceptor complexes decreases in the order zinc > cadmium > mercury. The coordination complexes of organomercury compounds are so unstable that none have been reported. This stability sequence is probably best illustrated by the behavior of the dimethyl derivatives with bipyridyl, as described by Coates and Green (9). The inability of organomercury compounds to form adducts may be ascribed to (a) stabilization of linear structure by d-s hybridization, (b) decrease in bond strength, (c) high energy of p states.

Noltes and Van Den Hurk (10) have found that increasing the electronegativity of the R group on zinc increases the tendency to form coordination complexes. Diphenylzinc readily forms complexes with ethyleneglycol dimethyl ether (diglyme) and triphenylphosphine, while di-n-butylzinc forms only a very weak complex with diglyme and none at all with triphenylphosphine. Thiele also noted that in going from methyl to ethyl or propyl in  $R_2Cd$ , the complexing tendency decreases strongly (11).

In the cyclic ether adducts,  $Me_2Zn \cdot O(CH_2)_n$ , the strength of the zinc-ether bond and tendency to form 1:2 adducts increases with n (12). The cause of these stability differences probably lies in the orientation and character of the oxygen orbitals, which vary with ring size of the ether. Also these cyclic ether adducts dissociate in solution with the amount of dissociation depending on the solvent.

In the complexes derived from arsenic or phosphorus containing ligands, it appears that  $d\pi-d\pi$  bonding is not important because the di-n-butylzinc complexes (Table III) with nitrogen containing ligands are more thermally stable than the ditertiary arsine complexes (10). Lewis and co-workers have recently considered the role of  $d\pi-d\pi$  bonding in the ditertiary arsine complexes of  $d^{10}$  metals unimportant in view of the high ionization potential of the non-bonding  $d^{10}$  shell of the metal atoms (13).

All of these adducts are less sensitive to oxygen and water than the free uncomplexed dialkyls.

### Anionic Complexes

Wanklyn reported the first anionic complex  $NaZnEt_3$  in 1853 (14). Most of these complexes reported up to now are organozinc complexes. A few examples include the anions  $ZnR_3^-$  (17,18),  $ZnR_2H^-$  (15,16),  $ZnR_4^{2-}$  (19),  $Zn(C\equiv CH)_4^{2-}$  (20), and  $Cd(C\equiv CH)_4$  (21). Organomercury compounds have very little tendency to form anionic complexes (22).

The first part of the paper is devoted to a general discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom. The second part is devoted to a detailed discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom.

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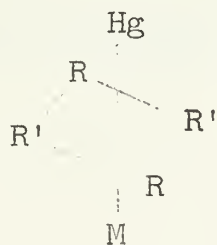
## Exchange Reactions

McCoy and Allred (23) have employed nuclear magnetic resonance along with equations developed by Gutowsky (24) to estimate the rate of methyl group exchange in the systems  $\text{Me}_3\text{Al}-\text{Me}_2\text{Cd}$ ,  $\text{Me}_2\text{Cd}-\text{Me}_2\text{Zn}$ ,  $\text{Me}_2\text{Zn}-\text{Me}_2\text{Hg}$ , and  $\text{Me}_2\text{Cd}-\text{Me}_2\text{Hg}$ . In the  $\text{Me}_3\text{Al}-\text{Me}_2\text{Cd}$  system, with benzene as solvent, rapid exchange occurs and the upper limit of the average lifetime  $\tau_A$  of a methyl group on a given metal atom is estimated to be 0.09 sec. In the  $\text{Me}_2\text{Cd}-\text{Me}_2\text{Zn}$  system rapid exchange also occurs, and the rate of exchange depends somewhat on concentration of the components. When the concentrations are greater than about one molar only one peak appears and  $\tau_A = 0.03$ , but in more dilute solutions two peaks appear corresponding to slower exchange. Using dilute solutions, McCoy and Allred demonstrated that the exchange rate is not greatly affected by solvent which ranged from dielectric constant 2 (cyclohexane) to 36.1 (pure nitrobenzene). It therefore appears that the rate-determining step is not primarily ionic.

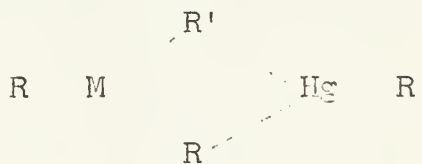
In the systems  $\text{Me}_2\text{Zn}-\text{Me}_2\text{Hg}$  and  $\text{Me}_2\text{Cd}-\text{Me}_2\text{Hg}$ , two resonance peaks appear with the sharpness and a separation comparable to that estimated from the pure components for no exchange.

Reutov (25), working with diphenylmercury-di-p-chlorophenylmercury<sup>203</sup>, reported mercury-mercury exchange involving four groups migrating simultaneously, since no  $\text{RHgR}'$  was found. However, it is not at all clear if Reutov specifically looked for the  $\text{RHgR}'$  species so this result seems doubtful.

In light of the above results, Dessy and co-workers decided to investigate the exchange pathway in more detail (26). They pictured two possible transition states, drawn out below, where the octahedral form would probably require the transfer of two

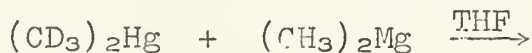


Octahedral



$S_F2$

groups from each metal during one interchange, thus providing no  $\text{EMR}'$  species, while the  $S_F2$  transition state would give rise to  $\text{EMR}'$ . By using mass spectrometry to study the particular system



1. Introduction

The first part of the paper discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study. The second part of the paper presents the results of the study and discusses the implications of the findings. The third part of the paper concludes the study and provides some final thoughts on the research.

The results of the study show that there is a significant relationship between the variables studied. This finding is consistent with the previous research in this area.

The study also found that the variables studied have a significant impact on the outcome variable. This finding has important implications for the field of study.

In conclusion, the study has shown that the variables studied are important and have a significant impact on the outcome variable. This finding is consistent with the previous research in this area.

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Dessy and co-workers were able to detect the presence of the species  $CD_3HgCH_3$ , which suggests the  $S_F2$  transition state is involved.

When mercury is one of the atoms involved, the methyl group exchange rate is slow. Also, coordinating solvents tend to increase the rate of exchange slightly, and this may be due to one or both of the following effects: (1) the activated complex may be stabilized by coordination, or (2) the carbon-metal bond may be weakened by coordination.

#### New Organometallic Compounds with Hg-Si, Hg-Ge, or Zn-Si Bonds

Bis(triphenylsilyl)zinc, the first compound containing a Zn-Si bond, was isolated by Wieberg and co-workers (29). It was prepared by reacting  $KSipH_3$  with  $ZnCl_2$  in liquid ammonia. Wieberg also reported the preparation of the compound bis(trimethylsilyl)mercury by shaking liquid  $Me_3SiBr$  with  $Na/Hg$  for several days. This is also the first compound containing a Hg-Si bond to be isolated, and further the first example of a volatile (sublimable) metal silyl. It is more stable than the corresponding carbon compound  $Hg(CMe_3)_3$ .

Some Russian workers (30) have reported the preparation of the compound bis(triethylgermanyl)mercury,  $(Et_3Ge)_2Hg$ , b.p.  $118-20^\circ$ , by heating  $Et_3GeH$  with  $Et_2Hg$  at  $100-120^\circ$ . However, reaction of  $Et_3SnH$  with  $Et_2Hg$  does not give the corresponding tin compound but the products  $Hg$ ,  $C_2H_6$ , and  $Et_3Sn_2$  (32).

Also the compounds  $EtHgSiEt_2SiEt_3$ ,  $Hg(SiEt_2SiEt_3)_2$ , and  $Et_3GeHgSiEt_3$  were prepared by some Russian workers (31). The first two were prepared by reacting  $Et_3SiSiEt_2H$  with  $Et_2Hg$  at  $160^\circ$  for 19 hours, and the third by reacting  $Et_3GeH$  with  $EtHgSiEt_3$  at  $100^\circ$  for 1 to 2 hours. Many of these compounds decompose when exposed to ultraviolet light.

It therefore appears that a whole new series of compounds is beginning to develop.



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# RECENT CORRELATIONS BETWEEN STRUCTURAL VARIATIONS IN A SERIES OF MOLECULES AND THEIR CHEMICAL PROPERTIES

Donald Dugre

November 24, 1964

## Introduction

Although relationships between structural variations in a series of molecules and their chemical properties have been known to organic chemists since 1924 (1), inorganic chemists have only recently become interested in similar correlations (2,3,4,5,6). The general form of the correlations found in the organic literature is

$$\ln \frac{k_i}{k_o} = AB \quad (I)$$

where  $k_i$  is the equilibrium or rate constant for the process under consideration and  $k_o$  is the equilibrium or rate constant for a standard reagent undergoing the same process. The constant A is a parameter which is characteristic of the difference between the standard reagent and the reagent under consideration and B is a constant characteristic of the reaction and reaction conditions. As we shall see in the following section, this is a linear free energy relation. Probably the most familiar equation of this type is the Hammett sigma-rho relation (7). Wells (8), Jaffe (9), Taft (10), and Leffler and Grunwald (11), among others, have reviewed the multitude of variations of the Hammett equation and their applications.

## Thermodynamic Effects

Consideration of equation I leads naturally to an examination of the thermodynamic effects involved in these correlations since

$$\ln K_{eq} = - \frac{\Delta F^o}{RT}$$

and

$$\ln k_{rate} = - \frac{\Delta F^\ddagger}{RT}$$

where  $\Delta F^o$  is the change in standard free energy due to a reaction and  $\Delta F^\ddagger$  is the free energy of activation. Then for a generalized constant K and a generalized free energy change,  $\Delta F$ , the relation between a member of the reaction series and the standard for the series is

$$\ln \frac{K_i}{K_o} = \frac{\Delta F_i}{\Delta F_o} = A_i B$$

Vol. 100, Part 1, 1970  
No. 1, 1970

CONTENTS  
The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

1. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

2. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

3. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

4. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

5. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

6. The Journal of the Royal Anthropological Institute, Vol. 100, Part 1, 1970, No. 1, 1970

which can be rearranged to give the linear relation

$$\Delta F_i = A_i B \Delta F_o$$

For two members (i,j) of a reaction series, we have

$$\ln \frac{K_i}{K_j} = \frac{\ln K_i / K_o}{\ln K_j / K_o} = \frac{\Delta F_i / \Delta F_o}{\Delta F_j / \Delta F_o} = \frac{A_i B}{A_j B}$$

and

$$\Delta F_i = \frac{A_i}{A_j} \Delta F_j$$

Since the linear free energy relations (L.F.E.R.) commonly used by organic chemists contain only two parameters, the analysis up to this point has considered only the effect due to a single change from the standard compound to the compound being compared. But, since the L.F.E.R. used by inorganic chemists contain four parameters, a more general analysis is needed.

Adopting the approach of Glasstone, Laidler and Eyring (12) and Wells (8), let us consider the effect of independent variables x, y, ... on the arbitrary free energy change  $\Delta F$  ( $\Delta F = f(x, y, \dots)$ )

$$d\Delta F = \left( \frac{\partial \Delta F}{\partial x} \right)_T dx + \left( \frac{\partial \Delta F}{\partial y} \right)_T dy + \dots$$

or taking  $x_o, y_o, \dots$  as arbitrary standards for the values of the variables x, y, ...

$$d\Delta F = \left( \frac{\partial \Delta F}{\partial x} \right)_T (x-x_o) + \left( \frac{\partial \Delta F}{\partial y} \right)_T (y-y_o) \dots$$

$$\left( \frac{\partial \Delta F}{\partial x} \right)_T = g_x \quad \text{and} \quad \left( \frac{\partial \Delta F}{\partial y} \right)_T = g_y$$

$$d\Delta F = g_x(x-x_o) + g_y(y-y_o) \dots$$

Considering only a single term, for two reactions A and B,

$$d\Delta F_A = g_x^A(x-x_o)$$

$$d\Delta F_B = g_x^B(x-x_o)$$

$$d\Delta F_B = \frac{g_x^A}{g_x^B} d\Delta F_A$$

Let  $f(x) = x^2 + 1$  and  $g(x) = x^2 - 1$ .

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

Expand the product using the distributive property.

$$= x^2(x^2 - 1) + 1(x^2 - 1)$$
$$= x^4 - x^2 + x^2 - 1$$
$$= x^4 - 1$$

$$f(x)g(x) = x^4 - 1$$

Factor the expression  $x^4 - 1$  using the difference of squares formula. The difference of squares formula states that  $a^2 - b^2 = (a + b)(a - b)$ . In this case,  $x^4$  is  $(x^2)^2$  and  $1$  is  $1^2$ . Therefore,  $x^4 - 1$  can be factored as  $(x^2 + 1)(x^2 - 1)$ .

Since  $f(x) = x^2 + 1$  and  $g(x) = x^2 - 1$ , the factored form of  $f(x)g(x)$  is  $(x^2 + 1)(x^2 - 1)$ .

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

Therefore, the factored form of the product  $f(x)g(x)$  is  $(x^2 + 1)(x^2 - 1)$ .

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

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$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

Thus, the factored form of the product  $f(x)g(x)$  is  $(x^2 + 1)(x^2 - 1)$ .

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$

$$f(x)g(x) = (x^2 + 1)(x^2 - 1)$$



or

$$\ln \left( \frac{K_i}{K_o} \right)_B = \frac{\frac{g_x^A T_B}{g_x^B T_A}}{\frac{g_x^A T_B}{g_x^B T_A}} \ln \left( \frac{K_i}{K_o} \right)_A$$

If the temperature at which reaction A occurs ( $T_A$ ) is equal to the temperature at which reaction B occurs ( $T_B$ ), and reaction series A is taken as a standard, then

$$\begin{aligned} \ln \frac{K_i}{K_o} &= \frac{g_x^A}{g_x^B} X_i \\ G_{AB} &= \frac{g_x^A}{g_x^B} X_i = \ln \left( \frac{K_i}{K_o} \right)_A \\ \ln \left( \frac{K_i}{K_o} \right)_B &= d \Delta F_B = G_{AB} X_i \quad (II) \end{aligned}$$

which is the usual two parameter correlation.

In order that the linear free energy relationship (II) exist between reaction series A and B, it is necessary that

- the ratio  $\frac{g_x^A}{g_x^B}$  remain constant over the range of variation of x.
- the ratio  $\frac{(X_i - X_o)_A}{(X_i - X_o)_B}$  remain constant
- only one variable X be involved.

Leffler and Grunwald (11) have obtained the same results using a different analysis. They show that  $G_{AB}$  is a function only of a term added to correct for the arbitrary separation of the standard free energy of the molecule into free energies of its constituent parts. In addition, they show that for a four parameter relation (two correction terms), there can be no cross terms such as

$$\left( \frac{\partial \Delta F}{\partial x \partial y} \right)_T$$

in the L.F.E.R. as it has been defined. Their results then require that for the case where two independent variables x and y are operating,

$$d \Delta F = G_x^{AB} X_i + G_y^{AB} Y_i$$

where  $G_y^{AB}$  and  $Y_i$  are defined in the same way as  $G_x^{AB}$  and  $X_i$ . Then the restrictions on the two parameter equation given above must apply to both terms simultaneously.

2.  $\frac{1}{x^2} = x^{-2}$

Derivative of  $x^{-2}$  is  $-2x^{-3} = -\frac{2}{x^3}$

$\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

$\frac{d}{dx} x^{-2} = -2x^{-3}$

10.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

11.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

12.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

13.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

14.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

15.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

16.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

$\frac{1}{x^2}$

17.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

18.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

19.  $\frac{d}{dx} \frac{1}{x^2} = -\frac{2}{x^3}$

Since

$$F = \Delta H - T \Delta S$$

$$d \Delta F = \left[ \frac{\partial \Delta H}{\partial x} \right]_T dx + \left[ \frac{\partial \Delta H}{\partial y} \right]_T dy - T \left[ \left[ \frac{\partial \Delta S}{\partial x} \right]_T dx + \left[ \frac{\partial \Delta S}{\partial y} \right]_T dy \right]$$

Then, in order that the previous restrictions a,b,c be valid, it is necessary that one of the following conditions holds for the two parameter equation:

$$d) \left[ \frac{\partial \Delta S}{\partial x} \right]_T = 0 \quad \text{isentropic series}$$

$$e) \left[ \frac{\partial \Delta H}{\partial x} \right]_T = 0 \quad \text{isenthalpic series}$$

$$f) \left[ \frac{\partial \Delta S}{\partial x} \right]_T = \beta \left[ \frac{\partial \Delta H}{\partial x} \right]_T \quad \text{isokinetic series}$$

Since the existence of any one of the restrictions d-f is not very probable, and since for the four-parameter LFER, it is necessary that the same restrictions be true for simultaneous variations in x and y, it is understandable that four-parameter LFER are comparatively rare.

### Two Parameter Linear Enthalpy Equation

Errede (2) has found that the dissociation energy  $D(X-Y)$  of a series of diatomic molecules can be 'reproduced' by the equation

$$D(X-Y) = L e_x e_y$$

where  $e_x$  is a parameter for X,  $e_y$  is a parameter for Y and L is characteristic of the type of bond between X and Y.

His method is to plot the bond energies  $D(R-X)$  versus the discrete variable parameter  $e_x$  which is chosen so that minimum scatter is obtained in the plots. (R = organic group, X = I, Br, Cl, H, F). The best straight lines are then chosen for each R series and the slope a, which is characteristic of the R group, is computed. He then considers molecules of the type  $(R_1-R_2)$  where each R is a  $CA_1A_2A_3$  group; A = (H, F, Cl, Br, I, or  $CX_3$ ) where the X's are as given above.  $e_1$  is then determined from the line for the  $D(R_1-X_1)$  series and  $e_2$  from the  $D(R_2-X_1)$  series. It is found that  $D(R_1-R_2)_1 = a_1 e_2 = a_2 e_1$  and therefore

$$\frac{a_1}{e_1} = \frac{a_2}{e_2} = L \quad (\text{a constant independent of R and X})$$

The first part of the paper is devoted to the study of the properties of the function  $f(x)$  defined by the equation

$f(x) = \int_0^x \frac{1}{1+t^2} dt$ . It is shown that  $f(x)$  is an increasing function and that  $f(x) < \frac{\pi}{2}$  for all  $x$ . The second part of the paper is devoted to the study of the function  $g(x)$  defined by the equation

$$g(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$$

$$g(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$$

$$g(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$$

It is shown that  $g(x)$  is a periodic function with period  $\pi$ . The third part of the paper is devoted to the study of the function  $h(x)$  defined by the equation

$$h(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$$

It is shown that  $h(x)$  is a periodic function with period  $\pi$ . The fourth part of the paper is devoted to the study of the function  $k(x)$  defined by the equation

$$k(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$$

It is shown that  $k(x)$  is a periodic function with period  $\pi$ . The fifth part of the paper is devoted to the study of the function  $l(x)$  defined by the equation

$l(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$ . It is shown that  $l(x)$  is a periodic function with period  $\pi$ . The sixth part of the paper is devoted to the study of the function  $m(x)$  defined by the equation

$m(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$ . It is shown that  $m(x)$  is a periodic function with period  $\pi$ . The seventh part of the paper is devoted to the study of the function  $n(x)$  defined by the equation

$n(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$ . It is shown that  $n(x)$  is a periodic function with period  $\pi$ . The eighth part of the paper is devoted to the study of the function  $o(x)$  defined by the equation

$o(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$ . It is shown that  $o(x)$  is a periodic function with period  $\pi$ . The ninth part of the paper is devoted to the study of the function  $p(x)$  defined by the equation

$p(x) = \int_0^x \frac{1}{1+t^2} dt - \frac{\pi}{2} x$ . It is shown that  $p(x)$  is a periodic function with period  $\pi$ . The tenth part of the paper is devoted to the study of the function  $q(x)$  defined by the equation

Errede is able to generate 986 new data from 49 parameters. The standard deviation is approximately 2%.

Neale (3) has found that it is possible to calculate  $e$  values for organic groups whose ionization potentials are known and for inorganic radicals whose ionization potentials ( $I$ ) and electron affinities ( $E$ ) are known. He separates the bonding groups into three classes:

A. groups in which unpaired electrons are localized on an atom other than carbon with non-bonded s or p electrons (primarily inorganic radicals)

$$e_A = 0.115(I_A - E_A) - 0.07$$

B. groups in which the unpaired electron is on carbon and is conjugated to an electron system ( $R-C\equiv C-CH_2\cdot$ ,  $HC\equiv C-CH_2\cdot$ , etc.)

$$e_B = 0.115I_B - 0.07$$

C. groups which do not fit into classes A or B ( $R_mH_{3-m}\cdot$ ,  $C_6H_5\cdot$ ,  $CH_2=CH\cdot$ ,  $H\cdot$ , etc.)

$$e_C = 0.0561I_C + 0.55$$

If we take the series  $R_0X$  as a standard and take everything relative to  $R_0X_0$ , then

$$D(R_0X) - D(R_0X_0) = (e_X - e_{X_0})Le_{R_0}$$

and for another reaction series

$$D(RX) - D(RX_0) = (e_X - e_{X_0})Le_R$$

thus

$$(20) \quad d\Delta H = D(RX) - D(R_0X) = (e_X - e_{X_0})L(e_R - e_{R_0}) = A_X B_R$$

where  $A_X = e_X - e_{X_0} = y - y_0$  and  $B_R = L(e_R - e_{R_0}) = \frac{d\Delta H}{dy}$

#### Four Parameter LFER

Edwards followed the lead of Swain and Scott (13) in attempting to find an LFER which took note of the fact that rates of displacements on alkyl carbon atoms do not follow the normal basicities of the attacking group (14,15,16). He found that many rate data for nucleophilic displacements and equilibria involving some degree of covalent bonding could be correlated by

$$\log \frac{K}{K_0} = \alpha E_n + \beta H. \quad (III)$$



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The constants  $\alpha$  and  $\beta$  are dependent on the identity of the substrate and  $\frac{K}{K_0}$  is a relative (to water) rate or equilibrium constant. The

constant  $E_n$  is the nucleophilicity constant of the donor and  $H$  is the basicity of the donor relative to the basicity of a proton. The nucleophilicity constant  $E_n$  is calculated from

$$E_n = E_0 + 2.60$$

where  $E^0$  is the electrode potential for oxidative dimerization of the donor and 2.60 represents the electrode potential for the oxidative dimerization of water. The relative basicity  $H$  is determined from

$$H = pK_a + 1.74$$

where  $pK_a$  is for the conjugate acid in aqueous solution and 1.74 is a correction for the  $pK_a$  of  $H_3O^+$ .

Ideally, it should be possible to get the  $\alpha$ 's and  $\beta$ 's for 58 substrates from 116 data and the  $E_n$ 's and  $H$ 's for 24 nucleophiles from 48 data and thus correlate an additional 1228 pieces of data, but because of lack of some vital numbers and in order to keep the error small, Edwards has used an unstated number of data in a least squares calculation.

In a later paper (5), Edwards redefined equation (III) in the following way:

$$E_n = aP + bH$$

$$P = \log \frac{R_{\infty}}{R_{H_2O, \infty}}$$

where  $R_{\infty}$  = molar refraction of nucleophile extrapolated to infinite wavelength and  $R_{H_2O, \infty}$  = molar refraction of water extrapolated to infinite wavelength. Thus

$$\log K/K_0 = AP + BH$$

where  $A = \alpha a$  and  $B = \beta + b\alpha$ . The immediate advantages of this redefinition are that the data for  $R_{\infty}/R_{H_2O, \infty}$  are easier to obtain than  $E_n$  and that commonly invoked dependence of the strength of electron donor-acceptor interactions on polarizability of the donor is explicitly given.

Analysis of Edwards' equation shows that it fits into the four parameter thermodynamic scheme given earlier, where

$$P = X_i, \quad A = G_x^{AB}, \quad H = Y_i, \quad B = G_y^{AB}.$$

THEORY OF THE EARTH AND ITS HISTORY  
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## Four Parameter Linear Enthalpy Relation

Wayland (6) recognized that a four parameter relation would be necessary to reproduce the observed reversal of relative heats of formation of certain Lewis acid-base combinations (17,18) (e.g.,  $(C_2H_5)_2O$  and  $(C_2H_5)_2S$  with  $I_2$  and  $C_6H_5OH$ ). Taking Mulliken's model of binding in charge-transfer complexes (19,20,21) as a starting point, he concluded that

$$\Delta H_{AB} = I_A I_B + C_A C_B$$

where  $I_B$  is the relative dipole moment of the base,  $C_B$  is the relative polarizability (as determined from molar refraction) of the base and  $I_A$  and  $C_A$  are constants characteristic of the acid. The terms  $I_A I_B$  and  $C_A C_B$  correspond roughly to electrostatic interaction between the acid and base and charge transfer interaction between the acid and base respectively. Using this treatment, Wayland has been able to generate 250 additional heats of formation with 88 parameters. The standard deviation for the correlation of 20 acid-base combinations cited in his thesis is 4% which is within experimental error.

An examination of the parameters  $I_B$  and  $C_B$  for the bases and  $I_A$  and  $C_A$  for the acids shows a striking similarity with Pearson's (22), and Pearson and Edwards' (23) qualitative discussion of "hard" and "soft" acids and bases. Taking bases whose polarizability (electron donating ability) term is large relative to their dipolar (coulombic interaction) term as soft, and defining hard bases and hard and soft acids in the same way, the phenomena of hard acids interacting most strongly with hard bases and soft acids interacting most strongly with soft bases is neatly rationalized. Moreover, Pearson and Edwards' discussion of the factors underlying these phenomena are perfectly consonant with most chemists' picture of the variation in properties for the donors and acceptors considered.

## Comments

It must be emphasized that none of the relationships discussed above presume to be an explanation or theory of the effect of structural changes on chemical properties. Their primary value at present is that they summarize a large number of data in a way that makes the trend in change of properties due to structural variations apparent. DeWar and Grisdale (24,25), Jaffe (26), and Sager and Ritchie (27) have attempted to give an explicit treatment (by molecular orbital theory) of the trends summarized by the Hammett equation, but they have not succeeded. Grunwald (28), Dewar (29), Sager and Ritchie (30) and Ehrenson (31) have recently discussed the problem of physical interpretation of IFER and similar relations.





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## SOME TRAPPED RADICAL STUDIES

Michael Garrett

December 15, 1964

### INTRODUCTION

In recent years, the technique of stabilization of free radicals through matrix isolation has been increasingly used in the identification and structural determination of these species. A book (1) and several short review articles (2, 3, 4, 5) have been written on various aspects of radical trapping.

The great advantages of matrix isolation are (1) the fact that a high concentration of radicals is present in the system for a long time, enabling spectroscopic techniques to be used (especially I-R) that could not be applied to gas or liquid phase problems and (2) the wide flexibility possible in generation of the species of interest.

Inert gas matrices are typically prepared by condensing the gas-phase reactive or reactant species with a large excess of the inert gas onto a cold surface. The latter is usually maintained at  $4^{\circ}$ - $20^{\circ}$ K. in order to prevent destruction of the radicals by diffusion through the lattice. Radicals may be generated in the gas phase prior to condensation by electrical or microwave discharges or high temperature ovens. The species of interest may be produced in situ by the decomposition of a trapped precursor. Methods used include photolysis, x-ray and electron bombardment. However, recombination due to the Brank-Rabinowitsch "cage effect" imposes limitations on the in situ production of radicals (see examples discussed below).

Matrix materials are not limited to simple gases; hydrocarbon and other organic glasses, formed by rapid condensation of the corresponding liquids, have been used for large organic radicals and ions (1), and radicals have been trapped in certain ionic crystals (4).

Once the radical has been trapped, it can be studied at leisure by methods which include I-R, optical and E.S.R. spectroscopy. Perturbations from "matrix effects" may be large and may cause splitting of the features, especially in optical spectroscopy. The analysis of such spectra is difficult, and even identification of the species may not be possible without outside information. Where gas phase spectra have been recorded, correlations with matrix bands are possible, but care must be exercised to distinguish "hot bands" which would not be expected to occur in matrix spectra because of the low temperature. Isotope shifts in I-R bands also provide useful information. Structural data is somewhat limited by the fact that, with the exception of a few hydride molecules, rotational fine structure is not observed in matrix spectra.

Attempts to explain the peculiarities of matrix spectra have met with mixed success. There is evidence of multiple trapping sites from E.S.R. studies of trapped H and alkali metal atoms in rare gas matrices (6, 7). The occurrence of satellite bands in electronic spectra of matrix isolated species has also been explained in terms of multiple sites (24). Most attempts to account for shifts in band

The first part of the report deals with the general situation of the country and the progress of the work during the year. It is followed by a detailed account of the various projects and the results achieved.

The second part of the report deals with the financial aspects of the work. It gives a detailed account of the income and expenditure for the year and shows how the funds have been used.

The third part of the report deals with the personnel of the organization. It gives a list of the staff and their duties and shows how they have contributed to the work of the organization.

The fourth part of the report deals with the future prospects of the organization. It gives an account of the plans for the next year and shows how the organization hopes to achieve its objectives.

The fifth part of the report deals with the conclusions of the year. It gives a summary of the main findings of the report and shows how they relate to the objectives of the organization.

The sixth part of the report deals with the appendices. It gives a list of the various documents and reports that have been used in the preparation of the report and shows how they have been used.



positions, especially in I-R spectra, are based on van der Waal's forces and exchange-repulsion (Pauli exclusion principle) forces (4, 5, 8, 9) (cf - "A Discussion of the Effect of Environment upon Molecular Energy Levels", Proc. Roy. Soc., A255, 1-31 (1960)). Aggregation, which can become important at the relatively high concentrations used in I-R work, and the far from perfect crystalline nature of most matrix deposits increase the complexity of the problem (1, 10, 33).

# SOME RECENT EXAMPLES OF MATRIX ISOLATION OF FREE RADICALS.

## HCO, DCO (11)

First triatomic, matrix-isolated radicals to be detected by I-R spectroscopy, these molecules were produced by photolysis of HI or HBr and DI or DBr in a CO matrix at 20°K. The optical spectrum was also recorded and results correlated with gas-phase measurements as a check in the identification of the species. This example differs from most in that the matrix itself is a reactant, a technique which the authors felt was "... an effective way of circumventing the inhibition of photolysis by the cage effect...."

## HO<sub>2</sub> (12)

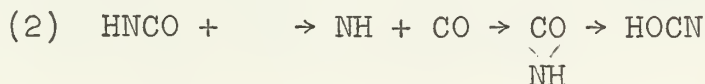
Another approach to the problem of recombination of radicals produced within the same trapping site is illustrated by work involving the elusive species HO<sub>2</sub>, which was produced by photolysis of HI or HBr and O<sub>2</sub> mixtures in an Ar matrix at 4°K. The H atoms arising from photolysis are sufficiently mobile to diffuse through the matrix and react with the O<sub>2</sub>. The use of DI, O<sup>18</sup> (100%) and O<sup>18</sup>-O<sup>16</sup> mixtures confirmed the assignment of the observed I-R peaks to HO<sub>2</sub>.

## KrF<sub>2</sub> (13)

Peaks appearing in the I-R spectra of an F<sub>2</sub>-Kr-Ar (1:70:220) mixture after photolysis at 20°K. were assigned to the molecule KrF<sub>2</sub>. XeF<sub>2</sub> was also prepared by the same method for comparison. No change was observed when F<sub>2</sub> and Ar were photolyzed alone.

## HOCN, DOCN (14)

These molecules were formed in situ upon photolysis at 4°K. or 20°K. of their stable tautomers HNCO and DNCO in an Ar or N<sub>2</sub> matrix. Determination of the structure of the absorber was by means of I-R spectra. For the mechanism of the rearrangement, which is of some interest, two mechanisms have been proposed:



The second route is favored because the mobility of the H atom should lead to the formation of NCO, which was not observed after prolonged photolysis.



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CF<sub>2</sub> (15, 16)

A third useful technique for the in situ production of trapped radicals involves the decomposition into the radical of interest plus a species of "special stability", so that recombination is inhibited. An example is the recent work on the photolysis of CF<sub>2</sub>N<sub>2</sub> in Ar and N<sub>2</sub> matrices, which leads to the production of CF<sub>2</sub> + N<sub>2</sub>. Optical and I-R spectra were taken, and from the C<sup>13</sup> (natural abundance) stretching frequency shifts a bond angle of 103° was estimated. Identification was made by correlation of matrix and gas-phase optical spectra. C<sub>2</sub>F<sub>4</sub> forms if diffusion is allowed to occur.

NH (1, 17)

This molecule has been studied repeatedly since it was first proposed to arise from the pyrolysis of HN<sub>3</sub>. The most recent effort was directed towards establishing a mechanism for the photolysis of HN<sub>3</sub> in solid matrices. Photolyses were carried out at 4°, ~14°, and 20°K. in Ar, N<sub>2</sub> and CO matrices. Identification was accomplished by the I-R and optical spectra and by the use of DN<sub>3</sub> and HN<sup>15</sup>N<sub>2</sub><sup>14</sup>. Photolysis of HN<sub>3</sub> is known to occur by cleavage of the HN...N<sub>2</sub> bond, but some evidence was formed for the cleavage of the H--N<sub>3</sub> bond as well. In the CO matrix, a high concentration of HCO in addition to HNCO was observed. Since HNCO and NH were not observed to undergo photolysis themselves, the H atoms which reacted to form HCO probably came directly from HN<sub>3</sub>.

NF, NCl, NBr, (18)

These species were produced in Ar or N<sub>2</sub> matrices at 4° or 20°K. by photolysis in situ of the corresponding halogen azide. Assignments were made for the I-R peaks of the parent FN<sub>3</sub>, ClN<sub>3</sub> and BrN<sub>3</sub> molecules as well as for the product HX. The correctness of these assignments was checked by the use of FN<sup>15</sup>-N<sub>2</sub><sup>14</sup>, and by the correspondence of the NBr frequency to that formed in gas phase spectra.

HBCl<sub>2</sub>, DBCl<sub>2</sub> (19)

Mixtures of BCl<sub>3</sub>-HBCl<sub>2</sub> and the deuterated species were trapped in Ar at ~10°K. in order to study conveniently their I-R spectra. Gas phase work is hampered by the disproportionation  $6\text{HBCl}_2 \rightleftharpoons 4\text{BCl}_3 + \text{B}_3\text{H}_6$ . Frequencies observed were compared to gas phase and calculated ones.

B<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>2</sub> (20)

These two species were trapped by condensing vapor effusing from an induction heated molybdenum knudsen cell with an excess of Ar or Xe. From the known vapor pressure of B<sub>2</sub>O<sub>3</sub> and the orifice geometry, it was possible to calculate concentrations in the matrix. The I-R spectrum of B<sub>2</sub>O<sub>3</sub> was analyzed in detail, using both natural boron (81.6% B<sup>11</sup>, 18.4% B<sup>10</sup>) and 100% B<sup>10</sup>. The V structure proposed on the basis of electron diffraction results was confirmed.

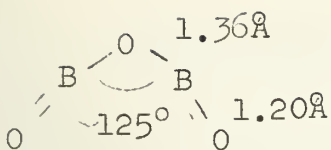
The first part of the paper is devoted to a general discussion of the problem. It is shown that the problem is of great importance in the theory of differential equations. The second part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The third part is devoted to the study of the asymptotic properties of the solutions of the problem. It is shown that the solutions of the problem have a certain asymptotic behavior as the independent variable tends to infinity.

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The eleventh part of the paper is devoted to the study of the asymptotic properties of the solutions of the problem. It is shown that the solutions of the problem have a certain asymptotic behavior as the independent variable tends to infinity. The twelfth part is devoted to the study of the properties of the solutions of the problem. It is shown that the solutions of the problem are unique and that they depend continuously on the data of the problem. The thirteenth part is devoted to the study of the asymptotic properties of the solutions of the problem. It is shown that the solutions of the problem have a certain asymptotic behavior as the independent variable tends to infinity.

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For  $B_2^{10}O_2$ , which was formed by heating  $B_2^{10}O_3$  with excess  $B^{10}$ , only one band was observed and a correlation was made to gas-phase emission I-R spectra. The molecule is apparently linear.

$C_2$ ,  $C_3$ ,  $C_n$

$C_2$  has been identified by Robinson and McCarty from its electronic absorption spectrum in matrices formed by condensing the products of a discharge through hydrocarbon vapor-rare gas mixtures (21). They observed only transitions from the  $^3\Pi_u$  state and concluded that this is the ground state of the molecule. However, Ramsay and Ballik (22) found  $^1\Sigma_g^+$  to be the ground state in the gas phase, and Ramsay noted that the metastability of  $^3\Pi_u$  re :  $^1\Sigma_g^+$  may have prevented the observation of the latter in the matrix (1).<sup>g</sup> Later, Schoen, who produced  $C_2$  by electron bombardment of trapped hydrocarbons, observed some electronic transitions which he designated as originating from the  $^1\Sigma_g^+$  state (23). These results were partially corroborated by Weltner (24),<sup>g</sup> who observed  $C_2$  bands after diffusion was allowed to occur in matrices containing  $C_3$ .

The latter species is a major constituent of carbon vapor (as determined mass-spectrometrically) and was trapped from high temperature vapor emitted from a carbon containing resistance heated Ta oven or from an induction heated carbon block (24, 25). Identification of  $C_3$  in the matrix was accomplished by I-R spectra and by electronic spectra in absorption and in fluorescence. Bands in the 4050 Å region arising from a  $^1\Sigma^+ \rightarrow ^1\Pi$  transition were correlated with recent gas phase measurements by Herzberg et.al. (26).

The very low value of  $V_2^{11} \simeq 70 \text{ cm}^{-1}$  calculated by Dixon (27) was verified (with reservations) and values for  $v_1''$ ,  $v_3''$ ,  $v_1'$ , and  $v_2'$  were given. A long lived emission observed at 5900 Å was taken to be  $^3\Pi_v \rightarrow ^1\Sigma_g^+$ .

Upon warm up, I-R bands appeared which were assigned to linear  $C_n$  species as discussed theoretically by Pitzer and Clementi (28).

$Si_2$ ,  $Si_3$ ,  $Si_4$  (29)

These species have been observed in Si vapor by mass spectrometry and were trapped in a similar way to  $C_3$ .  $Si_2$  was definitely identified by a correlation of the absorption spectrum to that observed in the gas phase (30, 31), and the ground state was shown to be  $^3\Sigma_g^-$ . Another series of bands, involving only one vibrational frequency ( $V_1'$ ) were assigned to  $Si_3$ , but this is tentative. A weaker series of bands is thought to be due to  $Si_4$ .





SiC<sub>2</sub>, Si<sub>2</sub>C, Si<sub>2</sub>C<sub>3</sub> (29)

These species were observed in matrices prepared by trapping the vaporization products of SiC.

Absorption bands due to SiC<sub>2</sub> were easily distinguished by correlations to gas phase spectra. Features missing in the matrix spectra were assumed to be "hot bands" and the analysis was corrected. I-R and emission spectra were also recorded. SiC<sub>2</sub> is linear and asymmetric and has a  $\frac{1}{2} \Sigma$  ground state similar to C<sub>3</sub>.

Two band systems at  $\sim 5300\text{\AA}$  and  $\sim 4900\text{\AA}$  were tentatively assigned to Si<sub>2</sub>C and another system to the species Si<sub>2</sub>C<sub>3</sub>. The latter molecule has been observed mass spectrometrically; evidence for its presence in the matrix is based upon the appearance of a progression with the characteristic stretching frequency of C<sub>3</sub>. The complexity of the I-R spectrum and the large number of progressions in the optical spectrum indicate that this molecule is the unsymmetrical SiSiC<sub>3</sub>.

The electronic configuration of these species was discussed in terms of Walsh's theory (32).

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(1911-1912)

The following is a list of the names of the persons who have been named in the records of the Board of Education, from the year 1911 to 1912, in the order in which they were named. The names are given in the order in which they were named, and are not in alphabetical order. The names are given in the order in which they were named, and are not in alphabetical order. The names are given in the order in which they were named, and are not in alphabetical order.

### APPENDIX

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# MICROPOTENTIOMETRIC STUDY OF CHLORIDE BINDING TO MOYOGLOBIN

Hassan Tayim

March 9, 1965

## Introduction

The effects of binding of small ions by protein molecules in solution have been manifested as anomalous results in some physico-chemical studies of the proteins in solution<sup>1,2,3</sup>. It has thus become essential to understand the nature and extent of such interactions. The present work deals with the detection and evaluation of the binding of chloride ions to sperm whale ferrimyoglobin in aqueous solution of potassium chloride and myoglobin.

The method applied is based on the reduction in the thermodynamic activity of the combining chloride ions in presence of protein in solution as determined by measurement of the free ion concentration by electromotive force method.

Although the e.m.f. method was applied to the investigation of reactions of proteins with acids and bases as early as 1898<sup>4</sup>, the binding by proteins of anions other than hydroxyl ions was first demonstrated by e.m.f. methods in 1932 by Hitchcock<sup>5</sup>. The first quantitative study of this sort, however, was made by Scatchard and co-workers (1950)<sup>6,7</sup>.

## Theoretical:

### (a) E.m.f. of Concentration Cell:

A concentration cell comprising two Ag/AgCl electrodes immersed in potassium chloride solutions of equal concentration (activity) has a zero e.m.f. If myoglobin solution is added to one of the two electrode compartments, the cell may develop an e.m.f. depending on the extent of chloride ion binding to myoglobin and on the effect of myoglobin on the liquid junction potential (Ej).

It can be shown that the e.m.f. of such a cell is given by

$$E = (RT/F)\ln(a_2/a_1) + E_j \text{ --- } (1)$$

with the electrode in the solution of lower activity being positive with respect to the other electrode, if  $E_j$  is zero or has the same polarity. For dilute solutions of protein equation (1) can be written as<sup>6</sup>

$$E = (RT/F)\ln(c_2/c_1) + E_j \text{ --- } (2)$$





(b) Theory of Anion Binding to Proteins:

Tanford<sup>8</sup> and Klotz<sup>9</sup> have shown that there are three general cases encountered in the treatment of the theory of binding:

- (i) For the simplest case where there are  $n$  identical independent (non interacting) sites on the protein molecule with  $n$  identical equilibrium constants, the average number of anions associated with each protein molecule ( $\bar{v}$ ) can be given from laws of chemical equilibria by

$$\bar{v}/(n-\bar{v}) = kc \quad \text{---} \quad (3)$$

where  $k$  is the overall association constant,  $c$  the concentration of free (unbound) chloride.

- (ii) When there are  $n$  identical sites, but binding at any one site affects the binding affinity at other sites, the average binding is given by

$$(\bar{v}/cf)\exp(2w\bar{v}) = K(n-\bar{v}) \quad \text{---} \quad (4)$$

$K$  being an intrinsic association constant and  $w$  the electrostatic interaction factor.

- (iii) In the more complicated case where there are different classes of binding sites, if  $n_1$  sites have intrinsic association constant  $K^{(1)}$ ,  $n_2$  sites have constant  $K^{(2)}$ , etc.--. in the absence of interaction between sites  $v$  is given by

$$\bar{v} = \frac{n_1 K^{(1)} c}{1 + K^{(1)} c} + \frac{n_2 K^{(2)} c}{1 + K^{(2)} c} + \text{-----} \quad (5)$$

and if there is interaction between sites,  $v$  is given by

$$\bar{v} = \frac{n_1 K^{(1)} c \exp(2w\bar{v})}{1 + K^{(1)} c \exp(2w\bar{v})} + \frac{n_2 K^{(2)} c \exp(2w\bar{v})}{1 + K^{(2)} c \exp(2w\bar{v})} \quad (6)$$

Experimental:

- (a) Electrodes: Ag/AgCl electrodes were prepared by electrolytically depositing silver on clean platinum electrodes from potassium silver cyanide solution, then partially chloridizing the silver layer by electrolytic oxidation in hydrochloric acid.

- (b) Concentration Cells:

A Y shaped cell was used after Scatchard<sup>6,7</sup>, with saturated potassium chloride bridge, especially in the work on serum albumin. A capillary junction cell, which is a modification of a cell used by Smith and Speakman<sup>10</sup> and Dunsmore and Speaksman<sup>11</sup> was used in the major part of the work. The

# THEORY OF THE EARTH'S CRUST

The theory of the earth's crust is a branch of geology which deals with the structure and composition of the upper part of the earth's crust.

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## 1. THE EARTH'S CRUST

The earth's crust is the uppermost layer of the earth. It is the part of the earth which is exposed to the atmosphere and is subject to the forces of erosion and weathering.

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## CONCLUSION

The theory of the earth's crust is a branch of geology which deals with the structure and composition of the upper part of the earth's crust. It is a branch of geology which deals with the structure and composition of the upper part of the earth's crust.

## REFERENCES

The theory of the earth's crust is a branch of geology which deals with the structure and composition of the upper part of the earth's crust. It is a branch of geology which deals with the structure and composition of the upper part of the earth's crust.

contact between the two solutions in the electrode compartments was produced at the end of a capillary tube. The junction was reproducible and caused no serious diffusion problems.

(c) Potentiometer-Electrometer Setup:

A highly sensitive K3 micropotentiometer (Leeds and Northorp) was used in conjunction with a locally designed and constructed vibrating reed electrometer.

## Results

The following observations were made:

- (1) The addition of myoglobin to chloride solution produced an e.m.f. in the opposite direction expected on basis of chloride binding to myoglobin. The e.m.f. increased with decreasing the pH of the system as expected by theoretical considerations.
- (2) Repeating the experiment of Scatchard<sup>6</sup> under experimental conditions almost identical to his, we arrived to the conclusion that the signs of the e.m.f.'s as reported by Scatchard and co-workers were actually reversed.
- (3) E.m.f. was measured for myoglobin + chloride/chloride system under conditions of minimum or no binding<sup>12</sup>. The results indicated that myoglobin (aside from binding) produces an e.m.f. of a sign opposite to the e.m.f. produced by binding. The latter could be calculated by applying a correction for the "liquid junction potential".
- (4) Myoglobin binds chloride ions at at least 20 sites as shown in the following table

| Myoglobin<br>concentration | Isoionic<br>pH | Chloride Binding Sites and their Constants |          |       |         |       |         |
|----------------------------|----------------|--|----------|-------|---------|-------|---------|
|                            |                | $n_1$                                      | $(k_1)$  | $n_2$ | $(k_2)$ | $n_3$ | $(k_3)$ |
| moles/l                    |                |  |          |       |         |       |         |
| 0.001                      | 6.47           | 1  | (15,000) | 6     | (100)   | 13    | (10)    |
| 0.0001                     | 6.25           | 1  | (50,000) | 6     | (5,000) | 13    | (20)    |

## Discussion

The results obtained can be correlated with the known structure of myoglobin: it is known from the work of Edmundson and Hirs<sup>3</sup> that the cationic groups on the myoglobin molecule include



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4 arginines, 12 hestidines and 19 lysines. It is also known from the work of Breslow and Gurd<sup>13</sup> that 6 of the hestidine groups are masked or inaccessible to interacting ions. The technique applied in the present work excludes the counting of the 4 arginines (normal pK greater than 12)<sup>14</sup>. Hence the 6 binding sites of intermediate binding affinity could be assigned to the 6 hestidine imidazolium groups, the 13 sites of weaker affinity to lysine amine groups, and the single site of the highest binding affinity to a special binding site on the myoglobin molecule. It has been actually reported by Stryer, Kendrew and Watson<sup>15</sup> that such a special site does exist.

In view of its structural similarity to myoglobin, hemoglobin posed an interesting case. A few measurements carried out in the course of the present investigation indicated, however, that it binds chloride ions to a much lesser extent than myoglobin. This may suggest that most of the cationic groups on the hemoglobin molecule are either of very weak binding affinity or inaccessible to interacting chloride ions.



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ALKYNE-BRIDGED TRANSITION  
METAL COMPLEXES

R. E. Wagner

April 13, 1965

Introduction

Since their discovery (1) these complexes have evoked many interesting questions. Their characterization presents a study of the application of spectral data and chemical reactions. These complexes are used as antiknocks in fuels (2), as starting materials in the preparation of other organometallic complexes (3, 4), and as catalysts in the cyclic trimerization of alkynes (5, 6).

Dinuclear Complexes

The dinuclear complexes containing one mono-alkyne molecule are summarized by the following generalized formulas.

- I.  $(CO)_3M(R-C_2-R^1)M(CO)_3$                        $M = Co$
- II.  $LM(R-C_2-R^1)ML$                                $M = Ni$ ;  $L =$  ligand containing  
cyclopentadienyl moiety
- III.  $M_2L_2(CO)_4(R-C_2-R^1)$                        $M = Mo$ ;  $L =$  cyclopentadienyl ion or  
tetraphenylcyclobutadiene

$R$  and  $R^1$  may be the same or different and may encompass a wide range of groups. (Table 1) The type of  $R$ -groups affects the physical and chemical properties and the method of preparation.

Physical Properties

The complexes are intensely colored solids or oily liquids. The solids are readily sublimable. The complex  $Co_2(CO)_8(F_3C-C_2-CF_3)$  sublimates at room temperature and atmospheric pressure. (7, 8) The substituents of the alkyne play an important role in determining the sensitivity to air oxidation. Tilney-Bassett (9) notes that for complexes of type II those derived from phenyl-substituted acetylenes are stable as solids, while those derived from alkyl-substituted acetylenes are slowly decomposed. Only the complexes derived from perfluoro-2-butyne are stable in nonpolar solvents. (8)

Preparation

The most common preparation of the cobalt complexes uses dicobalt



MEMORANDUM FOR THE RECORD

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TO: Mr. Tolson

FROM: Mr. Clegg

SUBJECT: [Illegible]

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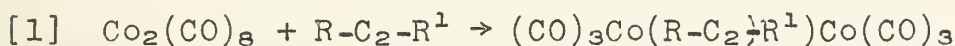
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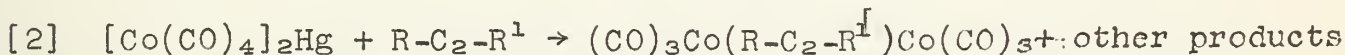
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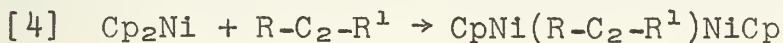
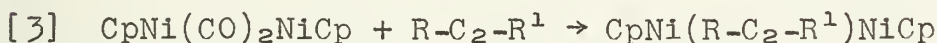
octacarbonyl and the appropriate acetylene. (1, 4, 8)



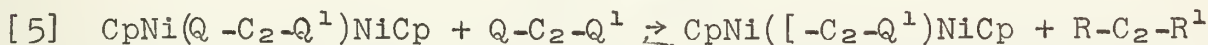
Under certain conditions, this reaction is quantitative. (1) Hübel noted that the products obtained depend on the temperature and on the substituents of the acetylenic molecule. (4) Kinetic studies have suggested a reactive form of  $\text{Co}_2(\text{CO})_8$ . (10, 22) There is no large variation in reaction rate with alkyl substituents ( $\text{R}$ ,  $\text{R}^1$ ). (11) A less favorable preparation is. (4, 12, 21)



Complexes of type II are prepared by the following reactions. (9, 8, 2, 37)



Dubeck (13) has shown that, when one or both of the R-groups is electron-withdrawing, the corresponding complex can be prepared by a replacement reaction.

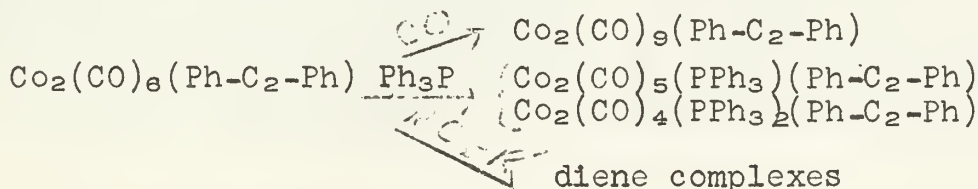


Attempts to prepare these complexes by 3. or 4. have either failed (9) or yielded complexes  $(\text{Q}-\text{C}_2-\text{Q}^1)\text{NiCp}_2$ . (14, 37)

The iron complexes  $\text{Fe}_2(\text{CO})_8(\text{R}-\text{C}_2-\text{R}^1)$  were considered to be analogous. (15, 16) A recent structure determination has disproved this assumption. (32, 33, 36) However, recent attempts to isolate less stable complexes have yielded complexes  $\text{Fe}_2(\text{CO})_7(\text{R}-\text{C}_2-\text{R}^1)$  which correspond formally to substitution products of  $\text{Fe}_2(\text{CO})_9$ . (34) The molybdenum complexes are the first reported examples of alkyne-bridged complexes containing other than a Group VIII transition metal. (17, 18, 19)

### Chemical Reactions

The complex  $\text{Co}_2(\text{CO})_8(\text{Ph}-\text{C}_2-\text{Ph})$  undergoes exchange with labeled CO at a much slower rate than its parent complex  $\text{Co}_2(\text{CO})_8$ . (20) Similarly a reduced reactivity to substitution by  $\text{P}(\text{Ph})_3$  has been noted. (21) Some reactions are shown below. (21, 4, 3, 23, 24)



(2) 20 1/2" diameter openings and the following:

$$q(\text{lb./sq. ft.}) = (175 - 100) \times 1.48 \times 10^{-4} \times 10^4 \quad (2)$$

1. The following is a summary of the data obtained from the tests conducted on the 20 1/2" diameter openings in the concrete slab.

(a) The load was applied in a uniform manner over the entire area of the opening. The load was applied in a uniform manner over the entire area of the opening.

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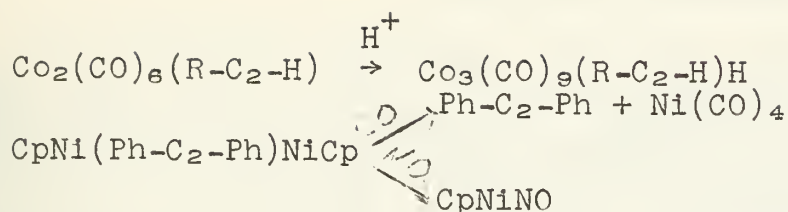
(l) The load was applied in a uniform manner over the entire area of the opening. The load was applied in a uniform manner over the entire area of the opening.

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## Structure

Degradative reactions have proven the existence of the unpolymerized "acetylenic" molecule in these complexes. However, the results do not unambiguously indicate the nature of the "acetylenic" bond. Much of the infrared data has been interpreted to indicate the double-bond character of the C-C bond and the absence of bridging CO-groups. (1, 4, 18) A crystal structure determination of  $\text{Co}_2(\text{CO})_8(\text{Ph}-\text{C}_2-\text{Ph})$  has shown the molecular skeleton to be as follows. (25)



A recent structure determination of the complex  $\text{Co}_2(\text{CO})_8(\text{C}_6\text{F}_5)$  shows a similar arrangement. (38)

With the exception of the complexes derived from fluorinated acetylenes (7, 8, 38), no significant shifts of the terminal CO-stretching vibrations have been noted. (1, 4, 26) Early work suggested that the number of CO-stretching vibrations could be correlated with the local symmetry (27) of the metal carbonyl fragments. Recent work by Bor (28), however, has suggested that the symmetry of the molecular skeleton is the determinant.

## Bonding

The bonding has been formally described by the Inert Gas rule. The alkyne molecule is considered a four-electron donor. Metal-metal bonding is postulated to account for the observed diamagnetism. The complexes  $\text{Fe}_2(\text{CO})_8(\text{R}-\text{C}_2-\text{R}^1)$  give an insight into the applicability of this rule. The structural parameters of the complex  $\text{Co}_2(\text{CO})_8(\text{Ph}-\text{C}_2-\text{Ph})$  do not unambiguously lead to an assignment of metal hybridization. (25, 29) The C-C bond distance makes a tetrahedral hybridization of the carbons seem unlikely. An approximate molecular orbital calculation based on a trigonal bipyramidal hybridization of the metal orbitals has been done. (29)



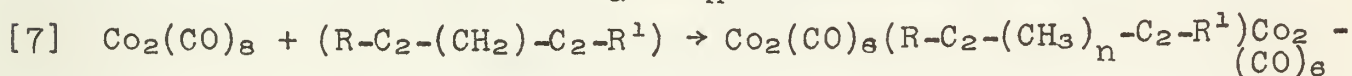
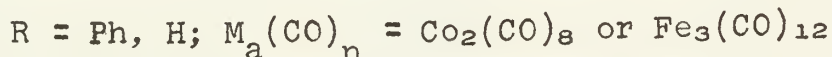
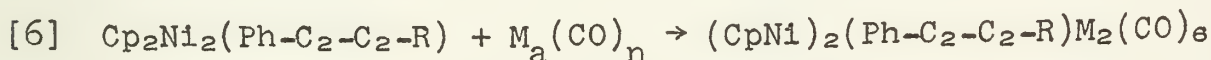


### Trinuclear Complexes

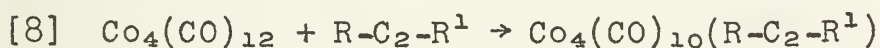
The trinuclear complexes which have been reported are listed in Table II. (15, 16, 30, 34) Their characterization has been scanty. The complexes are diamagnetic. Degradative reactions suggest that an unpolymerized "acetylenic" molecule is present. Recent attempts to isolate less stable complexes have yielded  $\text{Fe}_3(\text{CO})_9(\text{Ph-C}_2\text{-Ph})$ . (34) A recent structural determination has indicated that in one of the isomers of  $\text{Fe}_3(\text{CO})_9(\text{Ph-C}_2\text{-Ph})$  (16, 34), unpolymerized "acetylenic" molecules are acting as both  $\pi^-$  and  $\sigma^-$  donors. (34, 35)

### Tetranuclear Complexes

Tetranuclear complexes are of two types. In the first type, both triple bonds of a diynomolecule act as bridges (1, 6, 9, 30) Based on their diamagnetism, infrared spectra, and method of preparation, structures analogous to those of the dinuclear complexes have been proposed. These complexes are prepared by reactions 6 and 7.



The second type of tetranuclear complex contains one mono-alkyne molecule per molecule of complex. (30, 4) The cobalt complexes have been prepared in a manner formally analogous to the preparation of the dinuclear complexes. (4)



Two structures for the complex  $\text{Co}_4(\text{CO})_{10}(\text{Ph-C}_2\text{-Ph})$  have been proposed based on conflicting infrared spectra. (30, 4) A recent structural determination of the complex  $\text{Co}_4(\text{CO})_{10}(\text{Et-C}_2\text{-Et})$  has shown a distorted tetrahedral arrangement of the cobalt atoms. (39)

### Hexanuclear Complexes

Two hexanuclear complexes derived from 1,3,5-triethynylbenzene and 1,2,4-triethynylbenzene have been prepared. (6) The bonding in these complexes is believed to be similar to that in the dinuclear complexes.

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2. 1970-1971

Dinuclear Complexes

Table I

| Type I                          | $\text{Co}_2(\text{CO})_6(\text{R}-\text{C}_2-\text{R}^1)$            | Reaction | Reference |
|---------------------------------|---|----------|-----------|
| alkyne                          | m.p. °C   |          |           |
| phenylacetylene                 | (liq.)  | 1        | (1)       |
| isopropenylacetylene            | 31.8-32.8 <sup>a</sup>  | 1        | "         |
| propargyl alcohol               | 52.2-52.6 <sup>a</sup>  | 1        | "         |
| phenylpropionic acid            | 120 <sup>b</sup>  | 1        | "         |
| trimethylsilyl phenylacetylene  | 64  | 2        | (4)       |
| acetylene                       | 13.0-13.6 <sup>a</sup>  | 1        | (1)       |
| cyclodecyne                     | (liq.)  | 1        | "         |
| diphenylacetylene               | 109.5-110.0 <sup>a</sup>  | 1        | "         |
| perfluoro-2-butyne              | 114   | 1        | (7,8)     |
| diphenylbutadiyne               | 57-59   | 1        | (6)       |
| "perfluorocyclohex-1-yn-3-ene"  | 47-48   | -        | (38)      |
| Type II                         | $(\text{CpNi})_2(\text{R}-\text{C}_2-\text{R}^1)$                     |          |           |
| Acetylene                       | 143-44  | 3,4      | (2,9)     |
| 2-butyne                        | 55  | 3,4      | (2,9)     |
| perfluoro-2-butyne              | 91-93   | 3,4      | (2,9,37)  |
| diphenylbutadiyne               | 121   | 3        | (9)       |
| diphenylacetylene               | 149-150   | 3        | (9)       |
| phenylacetylene                 | 132-33  | 3        | (9)       |
| Type III                        | $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{R}-\text{C}_2-\text{R}^1)$ |          |           |
| L = cyclopentadienyl ion        |   |          |           |
| diphenylacetylene               | 239-40  | --       | (17,18)   |
| phenylacetylene                 | 138-39  | --       | (17,18)   |
| [L = tetraphenylcyclobutadiene] |   |          |           |
| diphenylacetylene               | 200-205 <sup>b</sup>  | --       | -(19)     |

a corrected

b melts with decomposition

TABLE 1

Continued

| TABLE 1 |   | Continued |      |
|---------|---|-----------|------|
|         |   |           |      |
| 1970    | 1 | 1970      | 1970 |
|         | 2 | 1970      | 1970 |
|         | 3 | 1970      | 1970 |
|         | 4 | 1970      | 1970 |
|         | 5 | 1970      | 1970 |
| 1971    | 1 | 1971      | 1971 |
|         | 2 | 1971      | 1971 |
|         | 3 | 1971      | 1971 |
|         | 4 | 1971      | 1971 |
|         | 5 | 1971      | 1971 |
| 1972    | 1 | 1972      | 1972 |
|         | 2 | 1972      | 1972 |
|         | 3 | 1972      | 1972 |
|         | 4 | 1972      | 1972 |
|         | 5 | 1972      | 1972 |
| 1973    | 1 | 1973      | 1973 |
|         | 2 | 1973      | 1973 |
|         | 3 | 1973      | 1973 |
|         | 4 | 1973      | 1973 |
|         | 5 | 1973      | 1973 |
| 1974    | 1 | 1974      | 1974 |
|         | 2 | 1974      | 1974 |
|         | 3 | 1974      | 1974 |
|         | 4 | 1974      | 1974 |
|         | 5 | 1974      | 1974 |
| 1975    | 1 | 1975      | 1975 |
|         | 2 | 1975      | 1975 |
|         | 3 | 1975      | 1975 |
|         | 4 | 1975      | 1975 |
|         | 5 | 1975      | 1975 |
| 1976    | 1 | 1976      | 1976 |
|         | 2 | 1976      | 1976 |
|         | 3 | 1976      | 1976 |
|         | 4 | 1976      | 1976 |
|         | 5 | 1976      | 1976 |
| 1977    | 1 | 1977      | 1977 |
|         | 2 | 1977      | 1977 |
|         | 3 | 1977      | 1977 |
|         | 4 | 1977      | 1977 |
|         | 5 | 1977      | 1977 |
| 1978    | 1 | 1978      | 1978 |
|         | 2 | 1978      | 1978 |
|         | 3 | 1978      | 1978 |
|         | 4 | 1978      | 1978 |
|         | 5 | 1978      | 1978 |
| 1979    | 1 | 1979      | 1979 |
|         | 2 | 1979      | 1979 |
|         | 3 | 1979      | 1979 |
|         | 4 | 1979      | 1979 |
|         | 5 | 1979      | 1979 |
| 1980    | 1 | 1980      | 1980 |
|         | 2 | 1980      | 1980 |
|         | 3 | 1980      | 1980 |
|         | 4 | 1980      | 1980 |
|         | 5 | 1980      | 1980 |
| 1981    | 1 | 1981      | 1981 |
|         | 2 | 1981      | 1981 |
|         | 3 | 1981      | 1981 |
|         | 4 | 1981      | 1981 |
|         | 5 | 1981      | 1981 |
| 1982    | 1 | 1982      | 1982 |
|         | 2 | 1982      | 1982 |
|         | 3 | 1982      | 1982 |
|         | 4 | 1982      | 1982 |
|         | 5 | 1982      | 1982 |
| 1983    | 1 | 1983      | 1983 |
|         | 2 | 1983      | 1983 |
|         | 3 | 1983      | 1983 |
|         | 4 | 1983      | 1983 |
|         | 5 | 1983      | 1983 |
| 1984    | 1 | 1984      | 1984 |
|         | 2 | 1984      | 1984 |
|         | 3 | 1984      | 1984 |
|         | 4 | 1984      | 1984 |
|         | 5 | 1984      | 1984 |
| 1985    | 1 | 1985      | 1985 |
|         | 2 | 1985      | 1985 |
|         | 3 | 1985      | 1985 |
|         | 4 | 1985      | 1985 |
|         | 5 | 1985      | 1985 |
| 1986    | 1 | 1986      | 1986 |
|         | 2 | 1986      | 1986 |
|         | 3 | 1986      | 1986 |
|         | 4 | 1986      | 1986 |
|         | 5 | 1986      | 1986 |
| 1987    | 1 | 1987      | 1987 |
|         | 2 | 1987      | 1987 |
|         | 3 | 1987      | 1987 |
|         | 4 | 1987      | 1987 |
|         | 5 | 1987      | 1987 |
| 1988    | 1 | 1988      | 1988 |
|         | 2 | 1988      | 1988 |
|         | 3 | 1988      | 1988 |
|         | 4 | 1988      | 1988 |
|         | 5 | 1988      | 1988 |
| 1989    | 1 | 1989      | 1989 |
|         | 2 | 1989      | 1989 |
|         | 3 | 1989      | 1989 |
|         | 4 | 1989      | 1989 |
|         | 5 | 1989      | 1989 |
| 1990    | 1 | 1990      | 1990 |
|         | 2 | 1990      | 1990 |
|         | 3 | 1990      | 1990 |
|         | 4 | 1990      | 1990 |
|         | 5 | 1990      | 1990 |
| 1991    | 1 | 1991      | 1991 |
|         | 2 | 1991      | 1991 |
|         | 3 | 1991      | 1991 |
|         | 4 | 1991      | 1991 |
|         | 5 | 1991      | 1991 |
| 1992    | 1 | 1992      | 1992 |
|         | 2 | 1992      | 1992 |
|         | 3 | 1992      | 1992 |
|         | 4 | 1992      | 1992 |
|         | 5 | 1992      | 1992 |
| 1993    | 1 | 1993      | 1993 |
|         | 2 | 1993      | 1993 |
|         | 3 | 1993      | 1993 |
|         | 4 | 1993      | 1993 |
|         | 5 | 1993      | 1993 |
| 1994    | 1 | 1994      | 1994 |
|         | 2 | 1994      | 1994 |
|         | 3 | 1994      | 1994 |
|         | 4 | 1994      | 1994 |
|         | 5 | 1994      | 1994 |
| 1995    | 1 | 1995      | 1995 |
|         | 2 | 1995      | 1995 |
|         | 3 | 1995      | 1995 |
|         | 4 | 1995      | 1995 |
|         | 5 | 1995      | 1995 |
| 1996    | 1 | 1996      | 1996 |
|         | 2 | 1996      | 1996 |
|         | 3 | 1996      | 1996 |
|         | 4 | 1996      | 1996 |
|         | 5 | 1996      | 1996 |
| 1997    | 1 | 1997      | 1997 |
|         | 2 | 1997      | 1997 |
|         | 3 | 1997      | 1997 |
|         | 4 | 1997      | 1997 |
|         | 5 | 1997      | 1997 |
| 1998    | 1 | 1998      | 1998 |
|         | 2 | 1998      | 1998 |
|         | 3 | 1998      | 1998 |
|         | 4 | 1998      | 1998 |
|         | 5 | 1998      | 1998 |
| 1999    | 1 | 1999      | 1999 |
|         | 2 | 1999      | 1999 |
|         | 3 | 1999      | 1999 |
|         | 4 | 1999      | 1999 |
|         | 5 | 1999      | 1999 |
| 2000    | 1 | 2000      | 2000 |
|         | 2 | 2000      | 2000 |
|         | 3 | 2000      | 2000 |
|         | 4 | 2000      | 2000 |
|         | 5 | 2000      | 2000 |
| 2001    | 1 | 2001      | 2001 |
|         | 2 | 2001      | 2001 |
|         | 3 | 2001      | 2001 |
|         | 4 | 2001      | 2001 |
|         | 5 | 2001      | 2001 |
| 2002    | 1 | 2002      | 2002 |
|         | 2 | 2002      | 2002 |
|         | 3 | 2002      | 2002 |
|         | 4 | 2002      | 2002 |
|         | 5 | 2002      | 2002 |
| 2003    | 1 | 2003      | 2003 |
|         | 2 | 2003      | 2003 |
|         | 3 | 2003      | 2003 |
|         | 4 | 2003      | 2003 |
|         | 5 | 2003      | 2003 |
| 2004    | 1 | 2004      | 2004 |
|         | 2 | 2004      | 2004 |
|         | 3 | 2004      | 2004 |
|         | 4 | 2004      | 2004 |
|         | 5 | 2004      | 2004 |
| 2005    | 1 | 2005      | 2005 |
|         | 2 | 2005      | 2005 |
|         | 3 | 2005      | 2005 |
|         | 4 | 2005      | 2005 |
|         | 5 | 2005      | 2005 |
| 2006    | 1 | 2006      | 2006 |
|         | 2 | 2006      | 2006 |
|         | 3 | 2006      | 2006 |
|         | 4 | 2006      | 2006 |
|         | 5 | 2006      | 2006 |
| 2007    | 1 | 2007      | 2007 |
|         | 2 | 2007      | 2007 |
|         | 3 | 2007      | 2007 |
|         | 4 | 2007      | 2007 |
|         | 5 | 2007      | 2007 |
| 2008    | 1 | 2008      | 2008 |
|         | 2 | 2008      | 2008 |
|         | 3 | 2008      | 2008 |
|         | 4 | 2008      | 2008 |
|         | 5 | 2008      | 2008 |
| 2009    | 1 | 2009      | 2009 |
|         | 2 | 2009      | 2009 |
|         | 3 | 2009      | 2009 |
|         | 4 | 2009      | 2009 |
|         | 5 | 2009      | 2009 |
| 2010    | 1 | 2010      | 2010 |
|         | 2 | 2010      | 2010 |
|         | 3 | 2010      | 2010 |
|         | 4 | 2010      | 2010 |
|         | 5 | 2010      | 2010 |
| 2011    | 1 | 2011      | 2011 |
|         | 2 | 2011      | 2011 |
|         | 3 | 2011      | 2011 |
|         | 4 | 2011      | 2011 |
|         | 5 | 2011      | 2011 |
| 2012    | 1 | 2012      | 2012 |
|         | 2 | 2012      | 2012 |
|         | 3 | 2012      | 2012 |
|         | 4 | 2012      | 2012 |
|         | 5 | 2012      | 2012 |
| 2013    | 1 | 2013      | 2013 |
|         | 2 | 2013      | 2013 |
|         | 3 | 2013      | 2013 |
|         | 4 | 2013      | 2013 |
|         | 5 | 2013      | 2013 |
| 2014    | 1 | 2014      | 2014 |
|         | 2 | 2014      | 2014 |
|         | 3 | 2014      | 2014 |
|         | 4 | 2014      | 2014 |
|         | 5 | 2014      | 2014 |
| 2015    | 1 | 2015      | 2015 |
|         | 2 | 2015      | 2015 |
|         | 3 | 2015      | 2015 |
|         | 4 | 2015      | 2015 |
|         | 5 | 2015      | 2015 |
| 2016    | 1 | 2016      | 2016 |
|         | 2 | 2016      | 2016 |
|         | 3 | 2016      | 2016 |
|         | 4 | 2016      | 2016 |
|         | 5 | 2016      | 2016 |
| 2017    | 1 | 2017      | 2017 |
|         | 2 | 2017      | 2017 |
|         | 3 | 2017      | 2017 |
|         | 4 | 2017      | 2017 |
|         | 5 | 2017      | 2017 |
| 2018    | 1 | 2018      | 2018 |
|         | 2 | 2018      | 2018 |
|         | 3 | 2018      | 2018 |
|         | 4 | 2018      | 2018 |
|         | 5 | 2018      | 2018 |
| 2019    | 1 | 2019      | 2019 |
|         | 2 | 2019      | 2019 |
|         | 3 | 2019      | 2019 |
|         | 4 | 2019      | 2019 |
|         | 5 | 2019      | 2019 |
| 2020    | 1 | 2020      | 2020 |
|         | 2 | 2020      | 2020 |
|         | 3 | 2020      | 2020 |
|         | 4 | 2020      | 2020 |
|         | 5 | 2020      | 2020 |
| 2021    | 1 | 2021      | 2021 |
|         | 2 | 2021      | 2021 |
|         | 3 | 2021      | 2021 |
|         | 4 | 2021      | 2021 |
|         | 5 | 2021      | 2021 |
| 2022    | 1 | 2022      | 2022 |
|         | 2 | 2022      | 2022 |
|         | 3 | 2022      | 2022 |
|         | 4 | 2022      | 2022 |
|         | 5 | 2022      | 2022 |
| 2023    | 1 | 2023      | 2023 |
|         | 2 | 2023      | 2023 |
|         | 3 | 2023      | 2023 |
|         | 4 | 2023      | 2023 |
|         | 5 | 2023      | 2023 |
| 2024    | 1 | 2024      | 2024 |
|         | 2 | 2024      | 2024 |
|         | 3 | 2024      | 2024 |
|         | 4 | 2024      | 2024 |
|         | 5 | 2024      | 2024 |
| 2025    | 1 | 2025      | 2025 |
|         | 2 | 2025      | 2025 |
|         | 3 | 2025      | 2025 |
|         | 4 | 2025      | 2025 |
|         | 5 | 2025      | 2025 |
| 2026    | 1 | 2026      | 2026 |
|         | 2 | 2026      | 2026 |
|         | 3 | 2026      | 2026 |
|         | 4 | 2026      | 2026 |
|         | 5 | 2026      | 2026 |
| 2027    | 1 | 2027      | 2027 |
|         | 2 | 2027      | 2027 |
|         | 3 | 2027      | 2027 |
|         | 4 | 2027      | 2027 |
|         | 5 | 2027      | 2027 |
| 2028    | 1 | 2028      | 2028 |
|         | 2 | 2028      | 2028 |
|         | 3 | 2028      | 2028 |
|         | 4 | 2028      | 2028 |
|         | 5 | 2028      | 2028 |
| 2029    | 1 | 2029      | 2029 |
|         | 2 | 2029      | 2029 |
|         | 3 | 2029      | 2029 |
|         | 4 | 2029      | 2029 |
|         | 5 | 2029      | 2029 |
| 2030    | 1 | 2030      | 2030 |
|         | 2 | 2030      | 2030 |
|         | 3 | 2030      | 2030 |
|         | 4 | 2030      | 2030 |
|         | 5 | 2030      | 2030 |
| 2031    | 1 | 2031      | 2031 |
|         | 2 | 2031      | 2031 |
|         | 3 | 2031      | 2031 |
|         | 4 | 2031      | 2031 |
|         | 5 | 2031      | 2031 |
| 2032    | 1 | 2032      | 2032 |
|         | 2 | 2032      | 2032 |
|         | 3 | 2032      | 2032 |
|         | 4 | 2032      | 2032 |
|         | 5 | 2032      | 2032 |
| 2033    | 1 | 2033      | 2033 |
|         | 2 | 2033      | 2033 |
|         | 3 | 2033      | 2033 |

Polynuclear Complexes

Table II

| Trinuclear Complexes  | m.p. °C              | Reaction | Reference |
|---|----------------------|----------|-----------|
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-Ph})\text{Fe}(\text{CO})_3$                  | 198-99               | -        | (30)      |
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-H})\text{Fe}(\text{CO})_3$                   | 121                  | -        | (30)      |
| $\text{Fe}_3(\text{CO})_{10}(\text{Ph-C}_2\text{-Me})$                            | -                    | -        | (15)      |
| $\text{Fe}_3(\text{CO})_9(\text{Ph-C}_2\text{-Ph})$                               | -                    | -        | (34)      |
| $\text{Fe}_3(\text{CO})_8(\text{Ph-C}_2\text{-Ph})_2$                             | 160 <sup>a</sup>     | -        | (16, 34)  |
| Tetranuclear Complexes  |                      |          |           |
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-Ph})\text{Fe}_2(\text{CO})_6$                | 180 <sup>a</sup>     | -        | (30)      |
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-H})\text{Fe}_2(\text{CO})_6$                 | 168 <sup>a</sup>     | -        | (30)      |
| $\text{Co}_4(\text{CO})_{10}(\text{Ph-C}_2\text{-Ph})$                            | 175-80 <sup>b</sup>  | 8        | (4)       |
| $\text{Co}_4(\text{CO})_{10}(\text{Et-C}_2\text{-Et})$                            | 160 <sup>b</sup>     | 8        | (4)       |
| $\text{Co}_4(\text{CO})_{10}(\text{Ph-C}_2\text{-CO}_2\text{-Me})$                | 145 <sup>b</sup>     | 8        | (4)       |
| $\text{Co}_4(\text{CO})_{12}(\text{Cl-C}_2\text{-(CH}_2)_6\text{-C}_2\text{-Cl})$ | 68-69                | 1        | (1)       |
| $(\text{CpNi})_4(\text{Ph-C}_2\text{-C}_2\text{-Ph})$                             | 296-97               | 3        | (9)       |
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-C}_2\text{-Ph})\text{Co}_2(\text{CO})_6$     | -----                | 6        | (9)       |
| $(\text{CpNi})_2(\text{Ph-C}_2\text{-C}_2\text{-Ph})\text{Fe}_2(\text{CO})_6$     | 156                  | 6        | (9)       |
| $[\text{Co}_2(\text{CO})_6]_2(\text{Ph-C}_2\text{-C}_2\text{-Ph})$                | 117-120 <sup>b</sup> | 7        | (5)       |
| Hexanuclear Complexes   |                      |          |           |
| $[\text{Co}_2(\text{CO})_6]_3\text{L}$  | 127-28 <sup>b</sup>  | -        | (6)       |
| $\text{L} \equiv 1,3,5\text{-triethynylbenzene}$                                  |                      |          |           |
| $[\text{Co}_2(\text{CO})_6]_3\text{L}^1$  | 120-130 <sup>b</sup> | -        | (6)       |
| $\text{L}^1 \equiv 1,2,4\text{-triethynylbenzene}$                                |                      |          |           |

a melts with decomposition

b decomposes



# Experimental results

## Experiment 1

| Condition | Variable | Value | Notes             |
|-----------|----------|-------|-------------------|
| 1         | 1        | 100   | Control condition |
| 2         | 2        | 100   | Control condition |
| 3         | 3        | 100   | Control condition |
| 4         | 4        | 100   | Control condition |
| 5         | 5        | 100   | Control condition |
| 6         | 6        | 100   | Control condition |
| 7         | 7        | 100   | Control condition |
| 8         | 8        | 100   | Control condition |
| 9         | 9        | 100   | Control condition |
| 10        | 10       | 100   | Control condition |
| 11        | 11       | 100   | Control condition |
| 12        | 12       | 100   | Control condition |
| 13        | 13       | 100   | Control condition |
| 14        | 14       | 100   | Control condition |
| 15        | 15       | 100   | Control condition |
| 16        | 16       | 100   | Control condition |
| 17        | 17       | 100   | Control condition |
| 18        | 18       | 100   | Control condition |
| 19        | 19       | 100   | Control condition |
| 20        | 20       | 100   | Control condition |
| 21        | 21       | 100   | Control condition |
| 22        | 22       | 100   | Control condition |
| 23        | 23       | 100   | Control condition |
| 24        | 24       | 100   | Control condition |
| 25        | 25       | 100   | Control condition |
| 26        | 26       | 100   | Control condition |
| 27        | 27       | 100   | Control condition |
| 28        | 28       | 100   | Control condition |
| 29        | 29       | 100   | Control condition |
| 30        | 30       | 100   | Control condition |
| 31        | 31       | 100   | Control condition |
| 32        | 32       | 100   | Control condition |
| 33        | 33       | 100   | Control condition |
| 34        | 34       | 100   | Control condition |
| 35        | 35       | 100   | Control condition |
| 36        | 36       | 100   | Control condition |
| 37        | 37       | 100   | Control condition |
| 38        | 38       | 100   | Control condition |
| 39        | 39       | 100   | Control condition |
| 40        | 40       | 100   | Control condition |
| 41        | 41       | 100   | Control condition |
| 42        | 42       | 100   | Control condition |
| 43        | 43       | 100   | Control condition |
| 44        | 44       | 100   | Control condition |
| 45        | 45       | 100   | Control condition |
| 46        | 46       | 100   | Control condition |
| 47        | 47       | 100   | Control condition |
| 48        | 48       | 100   | Control condition |
| 49        | 49       | 100   | Control condition |
| 50        | 50       | 100   | Control condition |
| 51        | 51       | 100   | Control condition |
| 52        | 52       | 100   | Control condition |
| 53        | 53       | 100   | Control condition |
| 54        | 54       | 100   | Control condition |
| 55        | 55       | 100   | Control condition |
| 56        | 56       | 100   | Control condition |
| 57        | 57       | 100   | Control condition |
| 58        | 58       | 100   | Control condition |
| 59        | 59       | 100   | Control condition |
| 60        | 60       | 100   | Control condition |
| 61        | 61       | 100   | Control condition |
| 62        | 62       | 100   | Control condition |
| 63        | 63       | 100   | Control condition |
| 64        | 64       | 100   | Control condition |
| 65        | 65       | 100   | Control condition |
| 66        | 66       | 100   | Control condition |
| 67        | 67       | 100   | Control condition |
| 68        | 68       | 100   | Control condition |
| 69        | 69       | 100   | Control condition |
| 70        | 70       | 100   | Control condition |
| 71        | 71       | 100   | Control condition |
| 72        | 72       | 100   | Control condition |
| 73        | 73       | 100   | Control condition |
| 74        | 74       | 100   | Control condition |
| 75        | 75       | 100   | Control condition |
| 76        | 76       | 100   | Control condition |
| 77        | 77       | 100   | Control condition |
| 78        | 78       | 100   | Control condition |
| 79        | 79       | 100   | Control condition |
| 80        | 80       | 100   | Control condition |
| 81        | 81       | 100   | Control condition |
| 82        | 82       | 100   | Control condition |
| 83        | 83       | 100   | Control condition |
| 84        | 84       | 100   | Control condition |
| 85        | 85       | 100   | Control condition |
| 86        | 86       | 100   | Control condition |
| 87        | 87       | 100   | Control condition |
| 88        | 88       | 100   | Control condition |
| 89        | 89       | 100   | Control condition |
| 90        | 90       | 100   | Control condition |
| 91        | 91       | 100   | Control condition |
| 92        | 92       | 100   | Control condition |
| 93        | 93       | 100   | Control condition |
| 94        | 94       | 100   | Control condition |
| 95        | 95       | 100   | Control condition |
| 96        | 96       | 100   | Control condition |
| 97        | 97       | 100   | Control condition |
| 98        | 98       | 100   | Control condition |
| 99        | 99       | 100   | Control condition |
| 100       | 100      | 100   | Control condition |

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1. The first part of the paper is devoted to a general discussion of the problem.

2. In the second part, we consider the case of a single particle.

3. The third part is devoted to the case of a system of particles.

4. In the fourth part, we consider the case of a continuous medium.

5. The fifth part is devoted to the case of a system of continuous media.

6. In the sixth part, we consider the case of a system of continuous media.

7. The seventh part is devoted to the case of a system of continuous media.

8. In the eighth part, we consider the case of a system of continuous media.

9. The ninth part is devoted to the case of a system of continuous media.

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13. The thirteenth part is devoted to the case of a system of continuous media.

14. In the fourteenth part, we consider the case of a system of continuous media.

15. The fifteenth part is devoted to the case of a system of continuous media.

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17. The seventeenth part is devoted to the case of a system of continuous media.

18. In the eighteenth part, we consider the case of a system of continuous media.



## The Transition-Metal Carbonyl Hydrides and Derivatives

Anton Schreiner

April 27, 1965

### A. Introduction

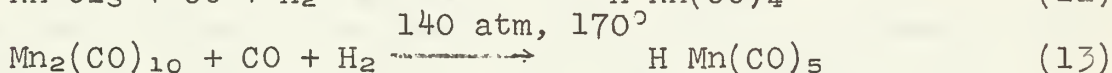
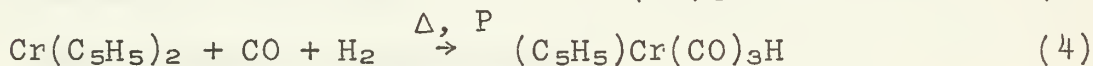
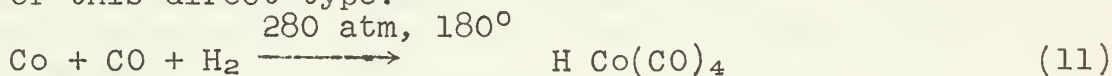
Numerous transition-metal carbonyl hydrides have been synthesized. In general, however, their properties have been incompletely characterized. It is attempted here to provide some insight into this area of chemistry.

### B. Representative Synthetic Methods and Properties

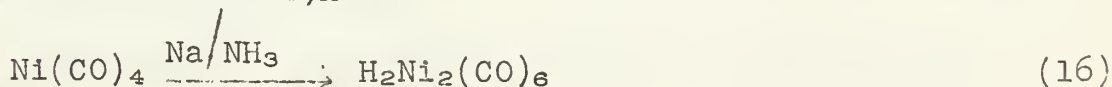
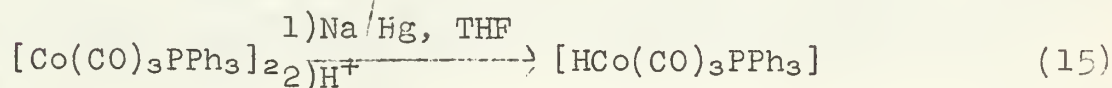
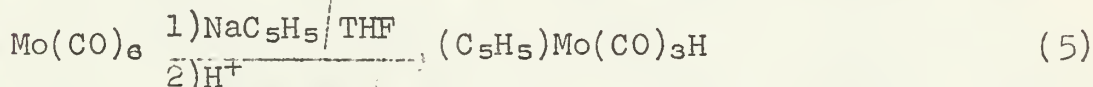
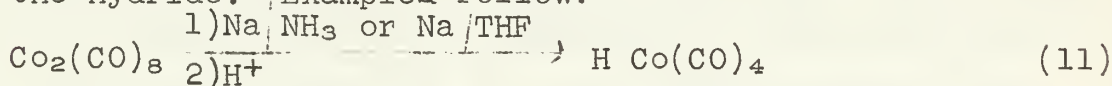
#### 1. Syntheses

There are four important preparative methods. The guiding principle of each is to retain the metal in a low oxidation state.

a. Direct Synthesis. The metal, one of its salts or a complex of the metal reacts with CO and H<sub>2</sub> under pressure and at elevated temperature. The following reactions are of this direct type:



b. Acidification of the Alkali Salts. In this series of reactions usually the metal carbonyl or a substituted metal carbonyl reacts with a solution of an alkali metal in liquid NH<sub>3</sub> (14) or Na/Hg in THF (5). The resulting sodium salt is then acidified to convert it to the hydride. Examples follow:



# THE HISTORY OF THE UNITED STATES

## CHAPTER I

The first chapter of the history of the United States is the story of the discovery of the continent by Christopher Columbus in 1492. This event marked the beginning of European exploration and settlement in North America.

## CHAPTER II

The second chapter of the history of the United States is the story of the early exploration and settlement of the continent. This period saw the arrival of the first European settlers and the beginning of the development of the colonies.

The third chapter of the history of the United States is the story of the growth and development of the colonies. This period saw the increasing number of settlers and the growing economic and political power of the colonies.

The fourth chapter of the history of the United States is the story of the American Revolution. This period saw the colonies fighting for independence from British rule and the establishment of the United States as a new nation.

The fifth chapter of the history of the United States is the story of the early years of the new nation. This period saw the challenges of building a new government and the early struggles of the United States.

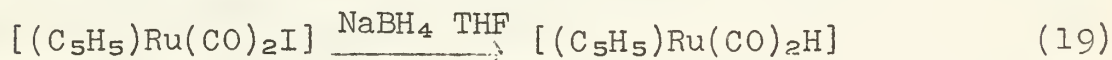
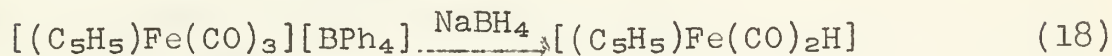
The sixth chapter of the history of the United States is the story of the expansion of the United States. This period saw the westward movement of settlers and the acquisition of new territories.

The seventh chapter of the history of the United States is the story of the Civil War. This period saw the United States divided over the issue of slavery and the ultimate triumph of the Union.

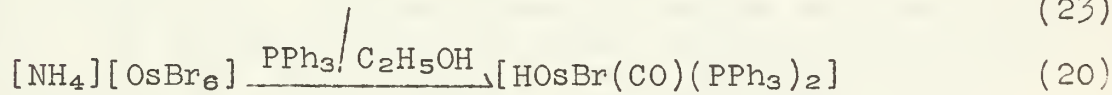
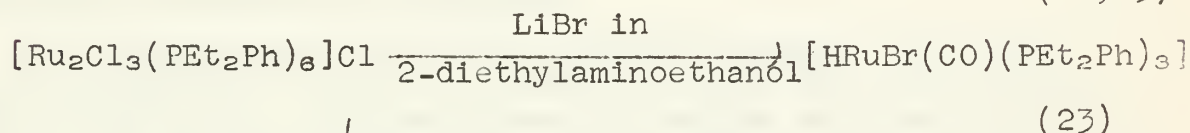
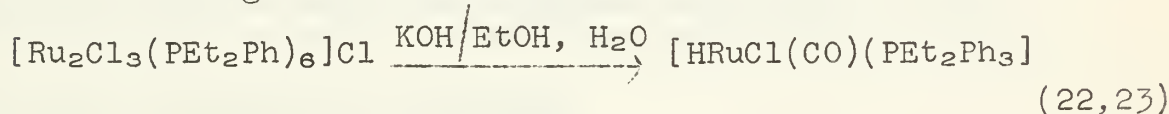
The eighth chapter of the history of the United States is the story of the Reconstruction period. This period saw the efforts to rebuild the South and integrate the freed slaves into the new nation.

The ninth chapter of the history of the United States is the story of the Gilded Age. This period saw the rapid industrialization and the rise of the wealthy elite.

c. Reduction with Hydrogenating Agents (11). Two reducing agents have been employed successfully, i.e.,  $\text{NaBH}_4$  and  $\text{LiAlH}_4$ . For example,



d. Reactions of Complexes with KOH Alcohol. Ligands CO and H are considered as originating from the alcohol (20,21). The following reactions illustrate this method



The fact that about 80 of these reactions have been observed to occur prompts the warning that alcohols often react more vigorously than is usually suspected (20). The above four methods have been responsible for obtaining most of the compounds of Table I.

## 2. Some Properties and Reactions

The compounds have been obtained as liquids, solids and gases. Some are only solution species (25). Table II presents melting points and colors of several compounds. Thermal stability ranges from below  $-70^\circ\text{C}$  to above  $100^\circ\text{C}$ , i.e.,  $\text{H}_2\text{Fe}(\text{CO})_4$  decomposes above  $-70^\circ\text{C}$ , while  $\text{HRe}(\text{CO})_5$  is a stable solid up to  $100^\circ\text{C}$ .

The acid properties of several species have been investigated. For example, the two acid constants of  $\text{H}_2\text{Fe}(\text{CO})_4$  are  $K_1 \approx 3.6 \times 10^{-5}$  and  $K_2 \approx 1 \times 10^{-14}$  at  $0^\circ\text{C}$  (26). On the other hand, the aqueous solution of  $\text{HMn}(\text{CO})_5$  is nearly neutral.

The reducing property (27) of these compounds makes them generally unstable towards air, whether in solution or in their natural state. Exceptions exist, as several carbonyl hydrides of osmium have shown very unusual oxidative and thermal stabilities. However, it is to be noted that they contain stabilizing substituted arsines or phosphines in the Os coordination sphere (20).

The compounds or their sodium salts are also of use as intermediates for syntheses of organometallic compounds and

1. The first step in the process of the investigation is to identify the problem. This is done by gathering information about the situation and the people involved.

2. The second step is to define the problem. This involves identifying the specific issues and the goals of the investigation.

3. The third step is to develop a plan of action. This involves determining the steps that need to be taken to solve the problem.

4. The fourth step is to implement the plan. This involves carrying out the steps that have been identified in the plan.

5. The fifth step is to evaluate the results. This involves assessing the effectiveness of the investigation and the actions taken.

6. The sixth step is to report the findings. This involves communicating the results of the investigation to the appropriate parties.

7. The seventh step is to follow up. This involves ensuring that the problem has been resolved and that the actions taken have been effective.

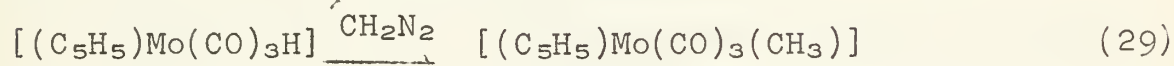
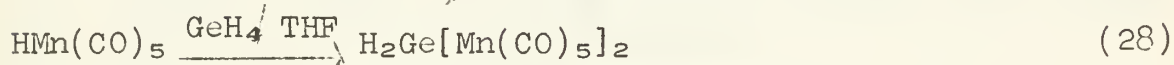
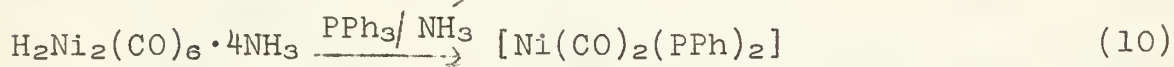
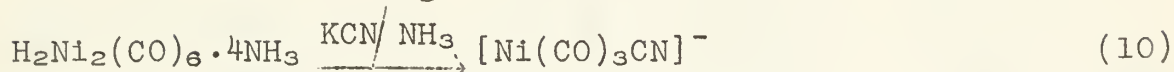
8. The eighth step is to document the process. This involves recording the steps taken and the results of the investigation.

9. The ninth step is to review the process. This involves evaluating the effectiveness of the investigation process and making improvements as needed.

10. The tenth step is to conclude the investigation. This involves finalizing the report and the actions taken.



others. The following reactions demonstrate this behavior:



It may be concluded that the chemical behavior of these compounds have not been investigated thoroughly. Their instability is probably the most important single reason.

### C. Structures and Aspects of Bonding

1. Diffraction and Other Data on Bond Lengths. The H atom has been directly located by diffraction in only one compound,  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ . The analogous Ir complex is isostructural with it, as concluded from its powder diffraction pattern (30). In fact, a total of only four carbonyl hydrides have been investigated by single crystal x-ray diffraction, i.e.,  $[\text{HMn}(\text{CO})_5]$ ,  $[\text{HOs}(\text{CO})\text{Br}(\text{PPh}_3)_3]$ ,  $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{PMe}_2)(\text{CO})_4]$  and the above  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ . Their structures appear below.

A rather interesting bond has been proposed by Doedens and Dahl in  $[(\text{C}_5\text{H}_5)_2\text{MoH}(\text{PMe}_2)(\text{CO})_4]$ . These workers propose (34) a "symmetrical, localized, bent three-center metal-hydrogen-metal bond". Similar bonding occurs in  $[\text{HMn}_2(\text{PPh}_2)(\text{CO})_8]$  and  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2\text{H}(\text{PR}_2)(\text{CO})_2]$ , these authors claim.

Electron diffraction studies of  $\text{H}_2\text{Fe}(\text{CO})_4$  and  $\text{HCo}(\text{CO})_4$  only show that the CO groups are tetrahedrally disposed with respect to the metal (resolution low) (35).

Semi-empirical LCAO-MO calculations (45,49) on  $\text{HCo}(\text{CO})_4$ , the symmetry of which will be discussed below, place the H atom ca. 1.2A from the Co (49).

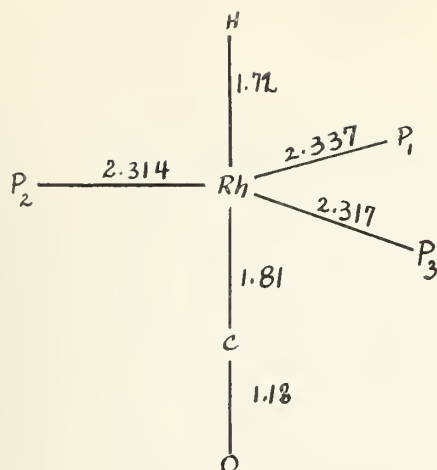
In one study broad-line NMR (37) was used to obtain the H-H interatomic distance (1.88A) in  $\text{H}_2\text{Fe}(\text{CO})_4$ . The Fe-H distance (1.1A) was calculated assuming a tetrahedral H-Fe-H bond angle (59).

At this point it seems desirable to evaluate the available data on transition metal-hydrogen bond distances. Regular covalent M-H bond distances are present in  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  (17) and in  $\text{K}_2\text{ReH}_9$  (115). The latter compound was advantageously studied by neutron diffraction. Refinements resulted in an average Re-H distance of  $1.68 \pm 0.01\text{A}$ .





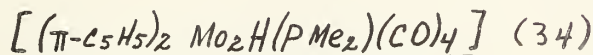
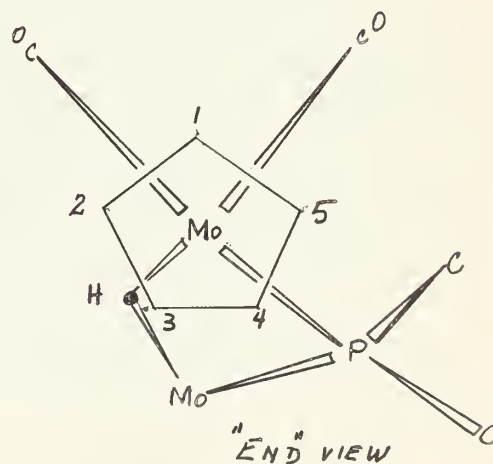
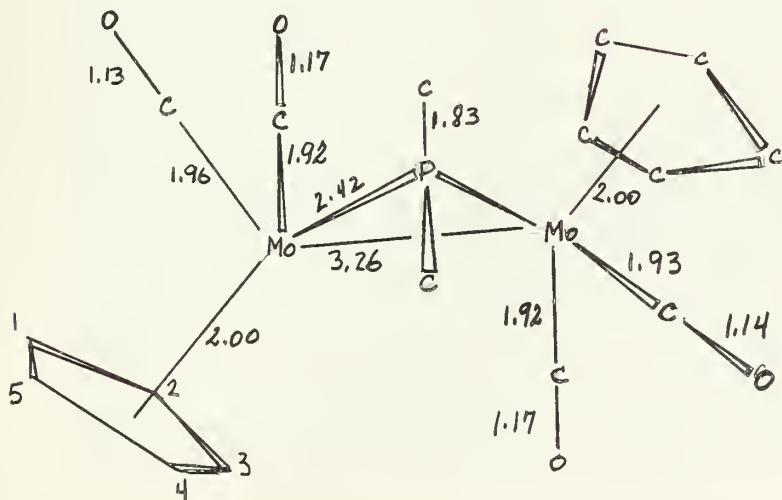
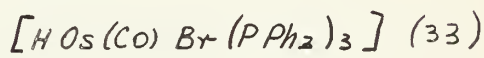
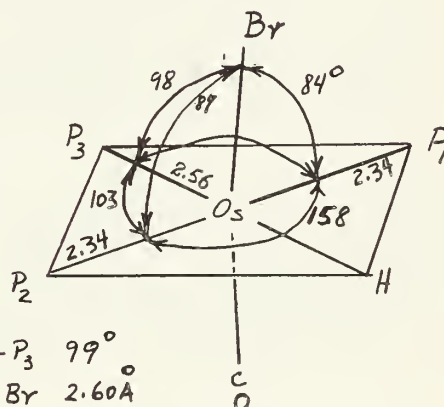
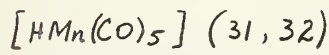
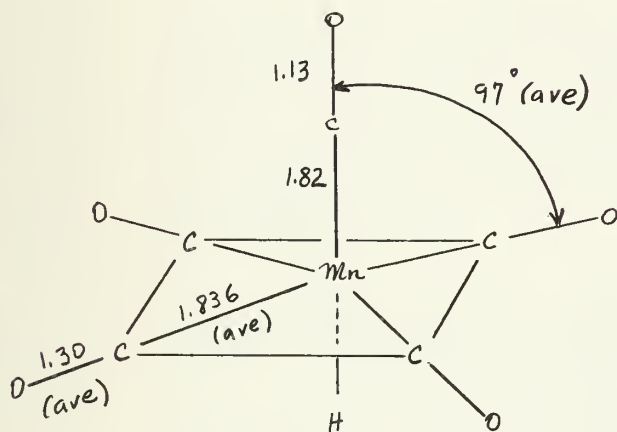
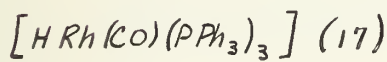
# REPORTED STRUCTURES



## ANGLES

|  |               |             |              |
|--|---------------|-------------|--------------|
| $P_1-Rh-P_2^*$                                     | $115.8^\circ$ | $OC-Rh-P_1$ | $94.8^\circ$ |
| $P_2-Rh-P_3$                                       | $120.6$       | $OC-Rh-P_2$ | $103.8$      |
| $P_2-Rh-P_1$                                       | $94.8$        | $OC-Rh-P_3$ | $98.0$       |
| $OC-Rh-P_3$ $170$ (PLANE NOT SPECIFIED BY AUTHORS) |               |             |              |

\* NUMBERING OF THE P ATOMS IS ASSUMED.





The Rh-H distance (1.72Å), on the other hand, was obtained from x-ray diffraction data (covalent radii are 1.43Å for Rh(60) and 0.30Å for H(61)). Refinements here resulted in a final R factor of 7.7% (Rh anisotropic refinement). Since the large phenyl groups in  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  lock the structure into place, the other isotropic refinements seem justified. These appear to be reliable data in support of a regular covalent M-H distance.

In contrast to the above evidence, some data appear to favor a M-H bond distance very much shorter than the sum of covalent radii. These distances are based on information obtained on the molecules  $\text{HCo}(\text{CO})_4$  (49),  $\text{H}_2\text{Mo}(\text{C}_5\text{H}_5)_2$  (116) and  $\text{H}_2\text{Fe}(\text{CO})_5$  (59).

In the first of these,  $\text{HCo}(\text{CO})_4$ , a ca. 1.2Å Co-H distance is concluded and based on the criterion of maximum total overlap between H, Co and C. However, this distance is not very certain because 1) the Co in the  $\text{Co}(\text{CO})_4$  portion is considered to be in a perfectly  $\text{Sp}^3$  hybridized state; 2) the proton is considered to be attached to the metal via the unmixed  $3d_{z^2}$  orbital of Co; 3) the uncertainty in the Slater exponents in Co.

In contrast to most publications on crystallographic results, the information about  $\text{H}_2\text{Mo}(\text{C}_5\text{H}_5)_2$  appears to be of a preliminary nature. The Mo-H distance is 1.2Å with an uncertainty of  $\pm 0.2$ Å, it was indicated (116), and is based on two-dimensional x-ray data. No anisotropic refinement was carried out, and the final R factor was 9.8%.

As mentioned above, the H-H distance in  $\text{H}_2\text{Fe}(\text{CO})_4$  was obtained from broad line NMR of the powder sample at 20°K. The intramolecular H-H distance was calculated to be  $1.88 \pm 0.05$ Å. The two H atoms were considered equivalent (one proton NMR line in liquid  $\text{H}_2\text{Fe}(\text{CO})_4$  (26)) and therefore the H-Fe-H angle different from  $90^\circ$ , in contrast to the requirements of an earlier model (117) which placed one proton on a lobe of pure  $3d_{x^2-y^2}$  and the other one on the  $3d_{z^2}$  orbital of Co. The H-Fe-H angle was then considered to be between a tetrahedral one and ca.  $125^\circ$ . Over this range of angles, one can compute Fe-H distances of 1.15Å ( $109^\circ 28'$ ) and 1.06Å ( $125^\circ 44'$ ) with a knowledge of the 1.88Å H-H distance. While suitable structures can be proposed for these angles, these authors (59) point out that "it is impossible to be precise regarding the H-Fe-H angle upon which the estimation of the Fe-H distance depends". For this reason the estimated Fe-H distance is 1.1Å. The broadening effect from  $\text{Fe}^{57}$  ( $I = 1/2$ ) in the  $\text{H}_2\text{Fe}$  part of the molecule was not considered in this work and intermolecular broadening neglected.

The first part of the paper is devoted to a study of the properties of the function  $f(x)$  defined by the equation  $f(x) = \sum_{n=0}^{\infty} a_n x^n$ , where  $a_n$  are the coefficients of the power series. It is shown that  $f(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $f(x) = x f(x^2)$ . The second part of the paper is devoted to a study of the properties of the function  $g(x)$  defined by the equation  $g(x) = \sum_{n=0}^{\infty} b_n x^n$ , where  $b_n$  are the coefficients of the power series. It is shown that  $g(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $g(x) = x g(x^2)$ .

The third part of the paper is devoted to a study of the properties of the function  $h(x)$  defined by the equation  $h(x) = \sum_{n=0}^{\infty} c_n x^n$ , where  $c_n$  are the coefficients of the power series. It is shown that  $h(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $h(x) = x h(x^2)$ . The fourth part of the paper is devoted to a study of the properties of the function  $k(x)$  defined by the equation  $k(x) = \sum_{n=0}^{\infty} d_n x^n$ , where  $d_n$  are the coefficients of the power series. It is shown that  $k(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $k(x) = x k(x^2)$ .

The fifth part of the paper is devoted to a study of the properties of the function  $l(x)$  defined by the equation  $l(x) = \sum_{n=0}^{\infty} e_n x^n$ , where  $e_n$  are the coefficients of the power series. It is shown that  $l(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $l(x) = x l(x^2)$ . The sixth part of the paper is devoted to a study of the properties of the function  $m(x)$  defined by the equation  $m(x) = \sum_{n=0}^{\infty} f_n x^n$ , where  $f_n$  are the coefficients of the power series. It is shown that  $m(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $m(x) = x m(x^2)$ .

The seventh part of the paper is devoted to a study of the properties of the function  $n(x)$  defined by the equation  $n(x) = \sum_{n=0}^{\infty} g_n x^n$ , where  $g_n$  are the coefficients of the power series. It is shown that  $n(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $n(x) = x n(x^2)$ . The eighth part of the paper is devoted to a study of the properties of the function  $o(x)$  defined by the equation  $o(x) = \sum_{n=0}^{\infty} h_n x^n$ , where  $h_n$  are the coefficients of the power series. It is shown that  $o(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $o(x) = x o(x^2)$ .

The ninth part of the paper is devoted to a study of the properties of the function  $p(x)$  defined by the equation  $p(x) = \sum_{n=0}^{\infty} i_n x^n$ , where  $i_n$  are the coefficients of the power series. It is shown that  $p(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $p(x) = x p(x^2)$ . The tenth part of the paper is devoted to a study of the properties of the function  $q(x)$  defined by the equation  $q(x) = \sum_{n=0}^{\infty} j_n x^n$ , where  $j_n$  are the coefficients of the power series. It is shown that  $q(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $q(x) = x q(x^2)$ .

The eleventh part of the paper is devoted to a study of the properties of the function  $r(x)$  defined by the equation  $r(x) = \sum_{n=0}^{\infty} k_n x^n$ , where  $k_n$  are the coefficients of the power series. It is shown that  $r(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $r(x) = x r(x^2)$ . The twelfth part of the paper is devoted to a study of the properties of the function  $s(x)$  defined by the equation  $s(x) = \sum_{n=0}^{\infty} l_n x^n$ , where  $l_n$  are the coefficients of the power series. It is shown that  $s(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $s(x) = x s(x^2)$ .

The thirteenth part of the paper is devoted to a study of the properties of the function  $t(x)$  defined by the equation  $t(x) = \sum_{n=0}^{\infty} m_n x^n$ , where  $m_n$  are the coefficients of the power series. It is shown that  $t(x)$  is a continuous function of  $x$  and that it satisfies the functional equation  $t(x) = x t(x^2)$ .



In view of these above data available on the transition-metal-hydrogen bond distances, it appears that the more direct and complete studies favor a regular covalent M-H distance.

2. Vibrational Spectroscopy. In general, terminal CO groups absorb in the range of 2000 to  $2100\text{ cm}^{-1}$ , bridging ones between  $1800$  to  $1900\text{ cm}^{-1}$ . The M-H stretching bond often occurs at approximately  $1900\text{ cm}^{-1}$ .

The vibrational spectrum of  $\text{HCo}(\text{CO})_4$ , for example, has been the subject of many interpretational studies (39, 40, 41, 42, 43, 44, 45, 46). The tetrahedral position of the CO groups has been assumed with the hydrogen attached 1) to the metal on a  $C_3$  axis (43, 44) or 2) to an oxygen colinear (35) or bent (40, 47) to the MCO axis. The best analysis of its vibrational spectrum favors the H lying on the  $C_3$  axis of the molecule and attached to the metal (44) which is in agreement with conclusions drawn from other investigations. The band at  $1934\text{ cm}^{-1}$  is assigned to the Co-H stretching mode ( $2.22 \times 10^5$  dynes / cm). The band at  $704\text{ cm}^{-1}$  corresponds to the Co-H bending motion. In addition, the following modes have been assigned (44): The C-O stretching fundamentals ( $2122$ ,  $2062$ ,  $2043\text{ cm}^{-1}$ ), the M-C-O bending modes ( $541$ ,  $467\text{ cm}^{-1}$ ) and Co-(CO) stretching frequencies ( $403$ ,  $330\text{ cm}^{-1}$ ). A normal coordinate analysis has not as yet been attempted to arrive at a reasonable force field.

The structure of  $[\text{HFe}(\text{CO})_4]^-$  (isoelectronic with  $\text{HCo}(\text{CO})_4$ ) is also of  $C_{3v}$  symmetry on the basis of its Raman spectrum (50).

Several authors have concluded a  $C_{4v}$  symmetry for  $\text{HMn}(\text{CO})_5$  (40, 51). This is in agreement with the  $\text{Mn}(\text{CO})_5$  skeletal structure in the solid state (see above). The analogous  $\text{HRe}(\text{CO})_5$  and  $\text{DRe}(\text{CO})_5$  exist and two bands at  $1832$  and  $1318\text{ cm}^{-1}$  were assigned to the Re-H and Re-D stretching vibrations (52).

These and other vibrational frequencies and their assignments appear in Table III below.

Polynuclear carbonyl hydrides have received less attention even though the use of local symmetry in analyzing their vibrational spectra simplifies the problem (53). The spectrum of the  $[\text{HRe}(\text{CO})_4]_3$  trimer was interpreted by Kaesz et al. in this manner (54). The molecule is of  $D_{3h}$  symmetry. The absence of a Re-H stretching frequency favors the structure with the H atoms placed symmetrically between Re atoms and in the plane of the latter.

Band assignments involving the CO parts of the molecules can be made by applying the approximations of Orgel (55) and Cotton (56) (see reference 57 for comments).



3. UV-Visible Spectral Data. The position of H in the spectrochemical series is between those of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . The following is an order of increasing ligand field strength:  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{OH}^- < \text{H}_2\text{O} < \text{H} < \text{NCS}^- < \text{NH}_3 < \text{NO}_2^-$ . This sequence has been concluded from the location of  $\lambda_{\text{max}}$  of d-d bands observed in the spectra of three series of compounds (58). One series is that of Table IV.

4. NMR Spectroscopy. Several authors have reported proton chemical shifts (or  $\delta$  values) of carbonyl hydrides. These shifts are large and several are presented in Table V below. They are invariably to the high-field side of TMS. In fact, in the absence of paramagnetic species, the presence of this high-field band is taken as being diagnostic of the transition metal-hydrogen bond.

An NMR application in elucidating molecular symmetry is the work on  $[\text{HRuCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$ . The compound was prepared, and the usual high-field band ( $\delta = 17.1$ ) was observed in the proton NMR spectrum. This band is split into two triplets (1:2:1) by P-H coupling as follows. The P trans to the H atom gives rise to the larger coupling constant ( $J_{\text{H-P}} = 107$  cps), and a doublet is expected. However, each component of this doublet is split into a triplet by the remaining two P nuclei ( $J_{\text{H-P}} = 24$  cps). This is interpreted to mean that the H and three P atoms are all in the same plane. The Br and CO ligands are above and below this plane.

Several theories have attempted to account for the high field shifts. One qualitative explanation was that the proton is buried in a non-bonding metal d-orbital. However, this is not plausible in view of the regular covalent Rh-H interatomic distance recently found (see above) in  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ .

The second qualitative model assumes the H to be hydride-like. Even a -1 charge on H, however, cannot account for a  $\delta$  value of 40, as  $\delta = 5$  for the  $\text{H}^{-1}$  ion (36).

Wilkinson et al. suggested that paramagnetic circulation at the metal atom, in addition to the local diamagnetic shielding at the hydrogen, would be experienced as a diamagnetic effect at H and account for the proton shift at high field. This explained the proton chemical shift in HI earlier (62).

Two quantitative treatments resulted from this latter suggestion. The first one is that of Stevens, Kern, Lsher and Lipscomb (1, 48). The more general model, however, is that of Buckingham and Stephens (36, 63). Both theories evaluate the contribution of the metal atom to the proton chemical shift and start with the Ramsey formula (62).

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Buckingham and Stephens arrive at the general expression

$$\sigma^{\text{total}} = \sigma_d^{\text{total}} + \frac{1}{3} (\sigma_{xx}^p + \sigma_{yy}^p + \sigma_{zz}^p),$$

$$\text{where } \sigma_d^{\text{total}} = \frac{e^2}{3mc^2} \left( \left\langle 0 \left| \sum_j \frac{r_{Hj}^2 + RZ_{Hj}}{r_{Hj}^3} \right| 0 \right\rangle \right)$$

and refers to the "diamagnetic" contribution and where, for example,

$$\sigma_{xx}^p = \frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \left\langle 0 \left| \sum_j \frac{1}{r_{Hj}} \right| n \right\rangle \cdot \left( n \left| \sum_K \frac{r_{HK}^{-3}}{r_{HK}} \right| 0 \right) + \text{Complex conjugate} \right\}$$

refers to part of the "paramagnetic" contribution to the total shielding constant.

With the Lipscomb model one evaluates only the diamagnetic contribution and neglects the paramagnetic term entirely. Its success, therefore, can only be attributed to  $\sigma^p$  being small in the several carbonyl hydrides considered.

In the more general treatment of Buckingham both diamagnetic and paramagnetic terms are evaluated. In these calculations only the first term in the above summation is retained and  $E_n$  taken from the lowest energy d-d transitions. Other parameters are  $R$  (M-H distance) and Slater's  $k$  ( $\chi_r = N r^{n-1} e^{-kr}$ ). It is predicted that the paramagnetic contribution is the largest by far in the total shielding ( $R = 2 \text{ a.u.}$ ,  $k \approx 3$ ,  $E_1 - E_0 = 25,000 \text{ cm}^{-1}$  for octahedral complexes).

Calculated shifts (both  $\sigma^d$  and  $\sigma^p$ ) by Buckingham and Stephens for some octahedral complexes (cis- $\text{MX}_4\text{H}_2$ , trans- $\text{MX}_4\text{YH}$ , trans- $\text{MX}_4\text{H}_2$ ,  $\text{MX}_5\text{H}$  and  $\text{MH}_6$ ) are much too low at M-H distances calculated from ordinary covalent radii. They therefore base their calculations on shorter M-H bond distances. However, the source of the discrepancy may lie in the approximate wave functions. It is very significant that the calculated  $\sigma^p$  is always about five times larger than  $\sigma^d$  for all reasonable values of  $k$  and  $R$ .





#### IV. Conclusion

It is evident that synthetic attempts have been quite successful in this area of inorganic chemistry. Table I, however, implies that many more compounds are still to be made. Their chemistry is also to be worked out more fully. Additional diffraction data are definitely needed to establish trends in structure. The latter information would then certainly make the quantitative interpretations of the data less approximate.

Page 100

The first part of the paper is devoted to a discussion of the general principles of the theory of the structure of the atom. It is shown that the structure of the atom is determined by the laws of quantum mechanics, and that the laws of quantum mechanics are in agreement with the experimental facts. The second part of the paper is devoted to a discussion of the specific properties of the atom, and the third part to a discussion of the applications of the theory of the structure of the atom.

Table I. Reported Compounds

| Vanadium Species  | References | Chromium Species   | References         |
|---|------------|--|--------------------|
| $[\text{HV}(\text{CO})_6]$  | 64         | $[\text{H}_2\text{Cr}(\text{CO})_5]$   | 65, 66             |
| $[\text{HV}(\text{CO})_5(\text{PPh}_3)]$                            | 64         | $[\text{HCr}(\text{CO})_5]^-$  | 67, 68, 69, 70, 66 |
|   |            | $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}]$   | 3, 4, 5, 1         |
|   |            | $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Cr}(\text{CO})_3\text{H}]^+$                            | 9                  |
|   |            | $[\text{HCr}_2(\text{CO})_{10}]^-$   | 70, 71, 72, 6      |
|   |            | $[\text{HCr}_2(\text{CO})_6(\text{OH})_3]^=$   | 73                 |
|   |            | $[\text{HCr}_2(\text{CO})_6(\text{CH}_3\text{O})]^=$   | 73                 |
| Molybdenum Species  | References | Tungsten Species   | References         |
| $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}]$            | 3, 5       | $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$  | 3, 5               |
| $[\text{HMo}_2(\text{CO})_{10}]^-$                                  | 6, 74, 1   | $[\text{HW}_2(\text{CO})_6(\text{OH})_3]^=$  | 78                 |
| $[\text{HMo}_2(\text{CO})_6(\text{OH})_3]^=$                        | 75         | $[\text{HW}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2]^+$   | 9                  |
| $[\text{H}_3\text{Mo}_2(\text{CO})_9(\text{OH})_3]$                 | 75         | $[\text{HW}_3(\text{CO})_9(\text{OH})(\text{OCH}_3)(\text{CH}_3\text{OH})]^=$                    | 78                 |
| $[\text{HMo}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2]^+$             | 9          | $[\text{H}_2\text{W}_2(\text{CO})_6(\text{H}_2\text{O})_2 \cdot \text{C}_6\text{H}_6]$           | 78                 |
| $[\text{HMo}_2(\text{CO})_4(\text{PMe}_2)(\text{C}_5\text{H}_5)_2]$ | 76, 77     | $[\text{H}_4\text{W}_4(\text{CO})_{12}(\text{H}_2\text{O})_4]$                                   | 78                 |
|   |            | $[\text{H}_4\text{W}_3(\text{CO})_9(\text{H}_2\text{O})(\text{OH})_2] \cdot 3\text{H}_2\text{O}$ | 79                 |
|   |            | $[\text{H}_4\text{W}_3(\text{CO})_9(\text{H}_2\text{O})(\text{OH})_2]$ anhyd.                    | 79                 |
|   |            | $[\text{H}_2\text{W}_3(\text{CO})_9(\text{OH})_2(\text{H}_2\text{O})]^=$                         | 79                 |
|   |            | $[\text{HW}_3(\text{CO})_9(\text{OH})_2(\text{H}_2\text{O})]^=$                                  | 79                 |
|   |            | $[\text{H}_4\text{W}_3(\text{CO})_9(\text{OH})(\text{OCH}_3)(\text{CH}_3\text{OH})]$             | 79                 |
|   |            | $[\text{H}_3\text{W}_3(\text{CO})_9(\text{OH})(\text{OCH}_3)(\text{CH}_3\text{OH})]^-$           | 79                 |
|   |            | $[\text{H}_3\text{W}_2(\text{CO})_6(\text{OH})_3]$   | 79                 |

# Table 1.1

| Category |    | Sub-category |        |
|----------|----|--------------|--------|
| A        | 1  | 1.1          | 1.1.1  |
|          | 2  | 1.2          | 1.2.1  |
|          | 3  | 1.3          | 1.3.1  |
|          | 4  | 1.4          | 1.4.1  |
|          | 5  | 1.5          | 1.5.1  |
|          | 6  | 1.6          | 1.6.1  |
|          | 7  | 1.7          | 1.7.1  |
|          | 8  | 1.8          | 1.8.1  |
|          | 9  | 1.9          | 1.9.1  |
|          | 10 | 1.10         | 1.10.1 |
| B        | 1  | 2.1          | 2.1.1  |
|          | 2  | 2.2          | 2.2.1  |
|          | 3  | 2.3          | 2.3.1  |
|          | 4  | 2.4          | 2.4.1  |
|          | 5  | 2.5          | 2.5.1  |
|          | 6  | 2.6          | 2.6.1  |
|          | 7  | 2.7          | 2.7.1  |
|          | 8  | 2.8          | 2.8.1  |
|          | 9  | 2.9          | 2.9.1  |
|          | 10 | 2.10         | 2.10.1 |
| C        | 1  | 3.1          | 3.1.1  |
|          | 2  | 3.2          | 3.2.1  |
|          | 3  | 3.3          | 3.3.1  |
|          | 4  | 3.4          | 3.4.1  |
|          | 5  | 3.5          | 3.5.1  |
|          | 6  | 3.6          | 3.6.1  |
|          | 7  | 3.7          | 3.7.1  |
|          | 8  | 3.8          | 3.8.1  |
|          | 9  | 3.9          | 3.9.1  |
|          | 10 | 3.10         | 3.10.1 |
| D        | 1  | 4.1          | 4.1.1  |
|          | 2  | 4.2          | 4.2.1  |
|          | 3  | 4.3          | 4.3.1  |
|          | 4  | 4.4          | 4.4.1  |
|          | 5  | 4.5          | 4.5.1  |
|          | 6  | 4.6          | 4.6.1  |
|          | 7  | 4.7          | 4.7.1  |
|          | 8  | 4.8          | 4.8.1  |
|          | 9  | 4.9          | 4.9.1  |
|          | 10 | 4.10         | 4.10.1 |



| Manganese Species   | References | Technitium Species   | References |
|---|------------|--|------------|
| [HMn(CO) <sub>5</sub> ]   | 80, 13     | [HTc(CO) <sub>5</sub> ]  | 87         |
| [DMn(CO) <sub>5</sub> ]   | 81, 82     | [HTc(CO) <sub>4</sub> ] <sub>3</sub> (?)   | 88         |
| [HMn(CO) <sub>4</sub> (PR <sub>3</sub> )]                                 | 83         |  |            |
| [H <sub>2</sub> Mn <sub>2</sub> (CO) <sub>9</sub> ]                       | 84         |  |            |
| [HMn(CO) <sub>4</sub> (PPh <sub>3</sub> )]                                | 85         |  |            |
| [HMn(CO) <sub>4</sub> (PEt <sub>3</sub> )]                                | 85         |  |            |
| [HMn(CO) <sub>4</sub> (P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> )] | 85         |  |            |
| [HMn(CO) <sub>4</sub> (P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )] | 85         |  |            |
| [HMn <sub>2</sub> (CO) <sub>8</sub> (PPh <sub>2</sub> )]                  | 86         |  |            |
| Rhenium Species   | References | Iron Species   | References |
| [HRe(CO) <sub>5</sub> ]   | 89         | [H <sub>2</sub> Fe(CO) <sub>4</sub> ]  | 92, 93     |
| [HRe(CO) <sub>4</sub> ] <sub>3</sub>                                      | 7          | [HFe(CO) <sub>4</sub> ] <sup>-</sup>   | 94         |
| [(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Re(CO) <sub>2</sub> H]     | 90         | [HDFe(CO) <sub>4</sub> ]   | 82         |
| [HRe <sub>2</sub> (CO) <sub>8</sub> O <sub>2</sub> ]                      | 91         | [HFe(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>                                  | 9          |
|   |            | [HFe(CO) <sub>5</sub> ] <sup>+</sup>   | 118        |
|   |            | [(C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> H]  | 96, 95, 18 |
|   |            | [(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sub>2</sub> (CO) <sub>4</sub> H] <sup>+</sup>       | 9          |
|   |            | [(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>2</sub> )H] | 97         |
|   |            | [(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sub>2</sub> (CO) <sub>2</sub> (PMe <sub>2</sub> )H] | 76         |
|   |            | [H <sub>2</sub> Fe <sub>2</sub> (CO) <sub>9</sub> ]  | 98         |
|   |            | [H <sub>2</sub> Fe <sub>3</sub> (CO) <sub>11</sub> ]   | 98         |
|   |            | [HFe <sub>3</sub> (CO) <sub>11</sub> ] <sup>-</sup>  | 98         |
|   |            | [H <sub>2</sub> Fe <sub>4</sub> (CO) <sub>13</sub> ]   | 99         |

| Left Hand Measurement |             | Right Hand Measurement |             |
|-----------------------|-------------|------------------------|-------------|
| Index                 | Measurement | Index                  | Measurement |
| 10                    | 1.000000    | 10                     | 1.000000    |
| 9                     | 0.999999    | 9                      | 0.999999    |
|                       |             | 8                      | 0.999998    |
|                       |             | 7                      | 0.999997    |
|                       |             | 6                      | 0.999996    |
|                       |             | 5                      | 0.999995    |
|                       |             | 4                      | 0.999994    |
|                       |             | 3                      | 0.999993    |
|                       |             | 2                      | 0.999992    |
|                       |             | 1                      | 0.999991    |

| Left Hand Measurement |             | Right Hand Measurement |             |
|-----------------------|-------------|------------------------|-------------|
| Index                 | Measurement | Index                  | Measurement |
| 10                    | 1.000000    | 10                     | 1.000000    |
| 9                     | 0.999999    | 9                      | 0.999999    |
| 8                     | 0.999998    | 8                      | 0.999998    |
| 7                     | 0.999997    | 7                      | 0.999997    |
| 6                     | 0.999996    | 6                      | 0.999996    |
| 5                     | 0.999995    | 5                      | 0.999995    |
| 4                     | 0.999994    | 4                      | 0.999994    |
| 3                     | 0.999993    | 3                      | 0.999993    |
| 2                     | 0.999992    | 2                      | 0.999992    |
| 1                     | 0.999991    | 1                      | 0.999991    |
| 0                     | 0.999990    | 0                      | 0.999990    |
| -1                    | 0.999989    | -1                     | 0.999989    |
| -2                    | 0.999988    | -2                     | 0.999988    |
| -3                    | 0.999987    | -3                     | 0.999987    |
| -4                    | 0.999986    | -4                     | 0.999986    |
| -5                    | 0.999985    | -5                     | 0.999985    |
| -6                    | 0.999984    | -6                     | 0.999984    |
| -7                    | 0.999983    | -7                     | 0.999983    |
| -8                    | 0.999982    | -8                     | 0.999982    |
| -9                    | 0.999981    | -9                     | 0.999981    |
| -10                   | 0.999980    | -10                    | 0.999980    |

| Ruthenium Species            | References        | Osmium Species                | References             |
|------------------------------|-------------------|-------------------------------|------------------------|
| $[(C_5H_5)Ru(CO)_2H]$        | 19                | $[HCo(CO)Cl(PEt_2Ph)_3]$      | 100                    |
| $[(C_5H_5)Ru(CO)_2D]$        | 19                | $[HOs(CO)Cl(PPh_3)_3]$        | 21, 24                 |
| $[HRu(CO)Cl(PPhEt_2)_3]$     | 22, 23            | $[DOs(CO)Cl(PPh_3)_3]$        | 21, 24                 |
| $[HRu(CO)Cl(PPh_3)_3]$       | 21                | $[HOsBr(CO)(PPh_3)_3]$        | 21, 24                 |
| $[HRu(CO)Br(PEt_2Ph)_3]$     | 23                | $[DOsBr(CO)(PPh_3)_3]$        | 21, 24                 |
| $[HRu(CO)I(PEt_2Ph)_3]$      | 23                | $[HOs(CO)Cl(AsPh_3)_3]$       | 24                     |
|                              |                   | $[DOs(CO)Cl(AsPh_3)_3]$       | 24                     |
|                              |                   | $[HOs(CO)Br(AsPh_3)_3]$       | 24                     |
|                              |                   | $[DOs(CO)Br(AsPh_3)_3]$       | 24                     |
| Cobalt Species               | References        | Rhodium Species               | References             |
| $[HCo(CO)_4]$                | 101, 102, 103, 11 | $[HRh(CO)_4]$                 | 12                     |
| $[DCo(CO)_4]$                | 82                | $[HRh(CO)(PPh_3)_3]$          | 17, 30, 105            |
| $[HCo(CO)_3PPh_3]$           | 104               |                               |                        |
| $[HCo(CO)_3(P(OC_6H_5)_3)]$  | 15                |                               |                        |
| Iridium Species              | References        | Nickel Species                | References             |
| $[HIr(CO)_4]$                | 106               | $[H_2Ni_4(CO)_9]$             | 111                    |
| $[HIr(CO)(PPh_3)_3]$         | 30, 107, 105      | $[HNi_4(CO)_9]^-$             | 10, 112, 113, 111, 114 |
| $[H_2Ir(CO)Cl(PPh_3)_2]$     | 108               | $[HNi_2(CO)_9]^-$             | 113                    |
| $[D_2Ir(CO)Cl(PPh_3)_2]$     | 108               | $[H_2Ni_2(CO)_6] \cdot 4NH_3$ | 14, 16                 |
| $[HIr(CO)Cl_2(PPh_3)_2]$     | 108, 109          | $[H_2Ni(CO)_3]$               | 38                     |
| $[HIr(CO)Cl_2(PPhEt_2)_2]$   | 110               |                               |                        |
| $[H_2Ir(CO)Cl_2(PPh_3)_3]Cl$ | 8                 |                               |                        |
| $[H_2Ir(CO)Br(PPh_3)_2]$     | 109               |                               |                        |



Table II. Melting Points and Colors of Some Carbonyl Hydrides

| Compound   | m.p.<br>(°C) | Color        |
|--|--------------|--------------|
| $[\text{HCo}(\text{CO})_4]$                              | -26          | yellow       |
| $[\text{H}_2\text{Fe}(\text{CO})_4]$                     | -70          | yellow       |
| $[\text{HMn}(\text{CO})_5]$                              | -24.6        | colorless    |
| $[\text{HRe}(\text{CO})_5]$                              | 100          | colorless    |
| $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}]$ | 57           | yellow       |
| $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}]$ | 54           | light yellow |
| $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$  | 69           | lemon yellow |
| $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}]$ | -10          | yellow       |
| $[\text{HRh}(\text{CO})_4]$                              | -12          | yellow       |
| $[\text{HRuCl}(\text{CO})(\text{PEtPh})_3]$              | 100          | white        |
| $[\text{HRuBr}(\text{CO})(\text{PEtPh})_3]$              | 110-113      | white        |
| $[\text{HRuI}(\text{CO})(\text{PEtPh})_3]$               | 141-143      | white        |
| $[\text{HOSCl}(\text{CO})(\text{PPh}_3)_3]$              | 179          | colorless    |
| $[\text{HOSBr}(\text{CO})(\text{PPh}_3)_3]$              | 172          | colorless    |
| $[\text{HOSCl}(\text{CO})(\text{AsPh}_3)_3]$             | 200          | colorless    |
| $[\text{HOSBr}(\text{CO})(\text{AsPh}_3)_3]$             | 195          | tan          |



# Table 1. Summary of the results of the analysis of variance for the different parameters of the different groups of subjects.

| Parameter | Group | Mean  | Standard deviation |
|-----------|-------|-------|--------------------|
| Age       | 1     | 25.5  | 2.5                |
| Age       | 2     | 26.5  | 2.5                |
| Age       | 3     | 27.5  | 2.5                |
| Age       | 4     | 28.5  | 2.5                |
| Age       | 5     | 29.5  | 2.5                |
| Age       | 6     | 30.5  | 2.5                |
| Age       | 7     | 31.5  | 2.5                |
| Age       | 8     | 32.5  | 2.5                |
| Age       | 9     | 33.5  | 2.5                |
| Age       | 10    | 34.5  | 2.5                |
| Age       | 11    | 35.5  | 2.5                |
| Age       | 12    | 36.5  | 2.5                |
| Age       | 13    | 37.5  | 2.5                |
| Age       | 14    | 38.5  | 2.5                |
| Age       | 15    | 39.5  | 2.5                |
| Age       | 16    | 40.5  | 2.5                |
| Age       | 17    | 41.5  | 2.5                |
| Age       | 18    | 42.5  | 2.5                |
| Age       | 19    | 43.5  | 2.5                |
| Age       | 20    | 44.5  | 2.5                |
| Age       | 21    | 45.5  | 2.5                |
| Age       | 22    | 46.5  | 2.5                |
| Age       | 23    | 47.5  | 2.5                |
| Age       | 24    | 48.5  | 2.5                |
| Age       | 25    | 49.5  | 2.5                |
| Age       | 26    | 50.5  | 2.5                |
| Age       | 27    | 51.5  | 2.5                |
| Age       | 28    | 52.5  | 2.5                |
| Age       | 29    | 53.5  | 2.5                |
| Age       | 30    | 54.5  | 2.5                |
| Age       | 31    | 55.5  | 2.5                |
| Age       | 32    | 56.5  | 2.5                |
| Age       | 33    | 57.5  | 2.5                |
| Age       | 34    | 58.5  | 2.5                |
| Age       | 35    | 59.5  | 2.5                |
| Age       | 36    | 60.5  | 2.5                |
| Age       | 37    | 61.5  | 2.5                |
| Age       | 38    | 62.5  | 2.5                |
| Age       | 39    | 63.5  | 2.5                |
| Age       | 40    | 64.5  | 2.5                |
| Age       | 41    | 65.5  | 2.5                |
| Age       | 42    | 66.5  | 2.5                |
| Age       | 43    | 67.5  | 2.5                |
| Age       | 44    | 68.5  | 2.5                |
| Age       | 45    | 69.5  | 2.5                |
| Age       | 46    | 70.5  | 2.5                |
| Age       | 47    | 71.5  | 2.5                |
| Age       | 48    | 72.5  | 2.5                |
| Age       | 49    | 73.5  | 2.5                |
| Age       | 50    | 74.5  | 2.5                |
| Age       | 51    | 75.5  | 2.5                |
| Age       | 52    | 76.5  | 2.5                |
| Age       | 53    | 77.5  | 2.5                |
| Age       | 54    | 78.5  | 2.5                |
| Age       | 55    | 79.5  | 2.5                |
| Age       | 56    | 80.5  | 2.5                |
| Age       | 57    | 81.5  | 2.5                |
| Age       | 58    | 82.5  | 2.5                |
| Age       | 59    | 83.5  | 2.5                |
| Age       | 60    | 84.5  | 2.5                |
| Age       | 61    | 85.5  | 2.5                |
| Age       | 62    | 86.5  | 2.5                |
| Age       | 63    | 87.5  | 2.5                |
| Age       | 64    | 88.5  | 2.5                |
| Age       | 65    | 89.5  | 2.5                |
| Age       | 66    | 90.5  | 2.5                |
| Age       | 67    | 91.5  | 2.5                |
| Age       | 68    | 92.5  | 2.5                |
| Age       | 69    | 93.5  | 2.5                |
| Age       | 70    | 94.5  | 2.5                |
| Age       | 71    | 95.5  | 2.5                |
| Age       | 72    | 96.5  | 2.5                |
| Age       | 73    | 97.5  | 2.5                |
| Age       | 74    | 98.5  | 2.5                |
| Age       | 75    | 99.5  | 2.5                |
| Age       | 76    | 100.5 | 2.5                |
| Age       | 77    | 101.5 | 2.5                |
| Age       | 78    | 102.5 | 2.5                |
| Age       | 79    | 103.5 | 2.5                |
| Age       | 80    | 104.5 | 2.5                |
| Age       | 81    | 105.5 | 2.5                |
| Age       | 82    | 106.5 | 2.5                |
| Age       | 83    | 107.5 | 2.5                |
| Age       | 84    | 108.5 | 2.5                |
| Age       | 85    | 109.5 | 2.5                |
| Age       | 86    | 110.5 | 2.5                |
| Age       | 87    | 111.5 | 2.5                |
| Age       | 88    | 112.5 | 2.5                |
| Age       | 89    | 113.5 | 2.5                |
| Age       | 90    | 114.5 | 2.5                |
| Age       | 91    | 115.5 | 2.5                |
| Age       | 92    | 116.5 | 2.5                |
| Age       | 93    | 117.5 | 2.5                |
| Age       | 94    | 118.5 | 2.5                |
| Age       | 95    | 119.5 | 2.5                |
| Age       | 96    | 120.5 | 2.5                |
| Age       | 97    | 121.5 | 2.5                |
| Age       | 98    | 122.5 | 2.5                |
| Age       | 99    | 123.5 | 2.5                |
| Age       | 100   | 124.5 | 2.5                |

Table III. Vibrational Frequencies (C-O, M-H, M-D) of Some  
Carbonyl Hydrides

| Compound   | $\nu_{\text{M-H}},$<br>$\text{cm}^{-1}$ | $\nu_{\text{M-D}}$ | $\nu_{\text{CO}}$    | Reference |
|--|---|--------------------|----------------------|-----------|
| $[\text{HRuCl}(\text{CO})(\text{PPh}_3)]$                | 2020                                    | 1457               | 1916<br>1916         | 21        |
| $[\text{HRuCl}(\text{CO})\text{PEt}_2\text{Ph}_3]$       | 1880                                    |                    | 1910                 | 23        |
| $[\text{HOSCl}(\text{CO})\text{PEt}_2\text{Ph}_3]$       | 2100                                    | 1505               | 1899<br>1880         | 21        |
| $[\text{HOSBr}(\text{CO})(\text{PEt}_2\text{Ph})_3]$     | 2105                                    | 1509               | 1902<br>1886         | 21        |
| $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}]$ | --                                      | --                 | 2030<br>1949<br>1913 | 5         |
| $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$  | --                                      | --                 | 2020<br>1929<br>1913 | 5         |
| $[\text{HPh}(\text{CO})(\text{P}(\text{Ph})_3)_3]$       | 2004                                    | --                 | 1926                 | 30        |
| $[\text{HIr}(\text{CO})(\text{PPh}_3)_3]$                | 2068                                    | --                 | 1930                 | 30        |
| $[\text{HRe}(\text{CO})_5]$                              | 1832                                    | 1318               | --                   | 52        |
| $[\text{HCo}(\text{CO})_4]$                              | 1934                                    |                    | 2122, 2062<br>2043   | 44        |



Table IV. The Electronic Spectra of  
trans - [Rhen<sub>2</sub>XCl]<sup>+</sup> Complexes (58)

| Complex Ion  | <sup>1</sup> A <sub>2g</sub> , <sup>1</sup> E <sub>g</sub> ← <sup>1</sup> A <sub>1g</sub> | <sup>1</sup> B <sub>2g</sub> , <sup>1</sup> E <sub>g</sub> ← <sup>1</sup> A <sub>1g</sub> |
|--|---|---|
| [Rhen <sub>2</sub> ICl] <sup>+</sup>                   | 22, 730 <sup>cm<sup>-1</sup></sup>  | ---   |
| [Rhen <sub>2</sub> BrCl] <sup>+</sup>                  | 24, 210   | ---   |
| [Rhen <sub>2</sub> ClCl] <sup>+</sup>                  | 24, 630   | 34, 970   |
| [Rhen <sub>2</sub> (H <sub>2</sub> O)Cl] <sup>+2</sup> | 26, 180   | 35, 710   |
| [Rhen <sub>2</sub> HCl] <sup>+</sup>                   | 27, 400   | ---   |
| [Rhen <sub>2</sub> (NCS)Cl] <sup>+</sup>               | 27, 550   | ---   |
| [Rhen <sub>2</sub> (NH <sub>3</sub> )Cl] <sup>+2</sup> | 29, 240   | 36, 360   |
| [Rhen <sub>2</sub> (NO <sub>2</sub> )Cl] <sup>+</sup>  | 32, 360   | ---   |





Table V.  $\tau$ -Values from Proton NMR Spectra  
of Some Carbonyl Hydrides

| Compound                                 | $\tau$ -Value for M-H Proton<br>(TMS = 10) |
|--|--|
| $\text{HMn(CO)}_5$                       | 17.5                                       |
| $\text{H}_2\text{Fe(CO)}_4$              | 21.1                                       |
| $\text{HCo(CO)}_4$                       | 20.0                                       |
| $\text{HFe}_3(\text{CO})_{11}^-$         | 24.9                                       |
| $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  | 24.9                                       |
| $\text{HCr(CO)}_3(\text{C}_5\text{H}_5)$ | 15.95                                      |
| $\text{HMo(CO)}_3(\text{C}_5\text{H}_5)$ | 15.65                                      |
| $\text{HW(CO)}_3(\text{C}_5\text{H}_5)$  | 17.65                                      |
| $\text{HFe(CO)}_2(\text{C}_5\text{H}_5)$ | 20.0                                       |



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CHAPTER 1

The first part of the book is devoted to a general discussion of the theory of the firm. It begins with a review of the basic concepts of microeconomics, such as the firm, the market, and the profit function. The author then discusses the various models of the firm, including the neoclassical model, the transaction cost model, and the resource-based view. The second part of the book is devoted to a detailed analysis of the firm's internal structure. It begins with a discussion of the firm's organization, including the hierarchy, the division of labor, and the coordination mechanisms. The author then discusses the firm's internal control system, including the monitoring and incentive systems. The third part of the book is devoted to a discussion of the firm's external environment. It begins with a discussion of the firm's relationship with its suppliers and customers. The author then discusses the firm's relationship with the government and the financial markets. The fourth part of the book is devoted to a discussion of the firm's strategic management. It begins with a discussion of the firm's mission and vision. The author then discusses the firm's strategic planning process, including the identification of opportunities and threats, the formulation of strategic goals, and the implementation of strategic actions. The fifth part of the book is devoted to a discussion of the firm's performance evaluation. It begins with a discussion of the firm's financial performance, including the calculation of the profit function. The author then discusses the firm's non-financial performance, including the measurement of the firm's social and environmental impact. The book concludes with a discussion of the firm's future prospects.

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(1) 
$$\frac{dx}{dt} = f(x, y, z), \quad \frac{dy}{dt} = g(x, y, z), \quad \frac{dz}{dt} = h(x, y, z),$$

where  $f, g, h$  are continuous functions of  $x, y, z$  in a domain  $D$  of the three-dimensional space.

2. In the second part we consider the case when the functions  $f, g, h$  are linear in  $x, y, z$  and the system (1) can be written in the form

(2) 
$$\frac{dx}{dt} = Ax + By + Cz, \quad \frac{dy}{dt} = Dx + Ey + Fz, \quad \frac{dz}{dt} = Gx + Hy + Iz,$$

where  $A, B, C, D, E, F, G, H, I$  are constants.

3. In the third part we consider the case when the functions  $f, g, h$  are quadratic in  $x, y, z$  and the system (1) can be written in the form

(3) 
$$\frac{dx}{dt} = Ax^2 + By^2 + Cz^2, \quad \frac{dy}{dt} = Dx^2 + Ey^2 + Fz^2, \quad \frac{dz}{dt} = Gx^2 + Hy^2 + Iz^2,$$

where  $A, B, C, D, E, F, G, H, I$  are constants.

4. In the fourth part we consider the case when the functions  $f, g, h$  are cubic in  $x, y, z$  and the system (1) can be written in the form

(4) 
$$\frac{dx}{dt} = Ax^3 + By^3 + Cz^3, \quad \frac{dy}{dt} = Dx^3 + Ey^3 + Fz^3, \quad \frac{dz}{dt} = Gx^3 + Hy^3 + Iz^3,$$

where  $A, B, C, D, E, F, G, H, I$  are constants.

5. In the fifth part we consider the case when the functions  $f, g, h$  are quartic in  $x, y, z$  and the system (1) can be written in the form

(5) 
$$\frac{dx}{dt} = Ax^4 + By^4 + Cz^4, \quad \frac{dy}{dt} = Dx^4 + Ey^4 + Fz^4, \quad \frac{dz}{dt} = Gx^4 + Hy^4 + Iz^4,$$

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118. A. F. Clifford and M. D. Campbell (Purdue) (work to be published).



Errata

| <u>Page</u> | <u>Printed Line</u> | <u>Corrected Reading</u>   |
|-------------|---------------------|--|
| 86          | 6                   | "...with <u>Basic Alcohol</u> ."   |
| 87          | 19                  | "...[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Mo <sub>2</sub> H(CO) <sub>4</sub> (PMe <sub>2</sub> )]." |
| 89          | 2                   | "...are <u>ca.</u> 1.27A..."   |
| 91          | 5 (from bottom)     | "...Kern, Lohr, Jr.,..."   |
| 92          | 11                  | "... <del>q</del> <sup>p</sup> ..."  |
| 92          | 17                  | "... $\psi_r = N r^{n^*-1} e^{-kr} \dots$ "  |



| 1914                       | 1914 | 1914 |
|----------------------------|------|------|
| "1914" 1914 1914           | 1    | 12   |
| 1914 1914 1914 (1914) 1914 | 11   | 12   |
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| 1914 1914 1914 1914        | 1    | 12   |

## RECENT CHEMISTRY OF PHOSPHOROCHLORIDES

V. Alan Mode

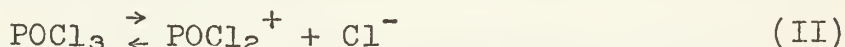
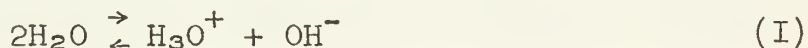
May 4, 1965

### Introduction

The recent interest in phosphorus chemistry has developed along two lines: (a) the study of phosphorus compounds by analogy to carbon chemistry and examination of the biochemical importance of organo-phosphorus compounds; (b) the study of phosphorus compounds as non-aqueous solvent systems for inorganic chemistry. This seminar will deal with some recent studies that developed from the non-aqueous solvent work and has employed the very similar behavior of four-coordinate phosphorus and analogous carbon compounds.

### POCl<sub>3</sub> Self-ionization

The use of POCl<sub>3</sub> as a non-aqueous solvent is extensively reported in the literature. In many cases, the observed chemistry has been explained by extension of the auto- or self-ionization concepts from aqueous systems:



In 1957, Lewis and Sowerby (1) reported experiments which cast considerable doubt on the importance of the ionization shown in equation (II). They were able to explain the observed radiochemical exchange reactions on the basis of a five-coordinate intermediate or transition state which did not involve self-ionization of POCl<sub>3</sub>.

### Five-Coordinate Phosphorus

A five-coordinate state of phosphorus is not unexpected. Compounds of the type PA<sub>5</sub> (e.g. PCl<sub>5</sub>) have been known and studied for years. Substitution reactions in four-coordinate phosphorus have been shown to occur via a five-coordinate state (2,3,4). It was further shown by Green and Hudson (5) that substitution and exchange reactions proceed by the same mechanism. During racemization of methyl ethyl-phenylphosphinate, methoxide exchange was also determined. The rate of racemization was twice the rate of exchange and the overall exchange was second order as would be predicted if the mechanism was one of a five-coordinate transition state where the phosphorus compound was undergoing a "Walden"-type inversion.

The possibility of a stable five-coordinate intermediate has been eliminated (6,7). While this work does not define a specific transition configuration, it did show that the life time of the five-coordinate state was much less than the period required for proton migration between similar oxygens in the compound.

MEMORANDUM FOR THE RECORD

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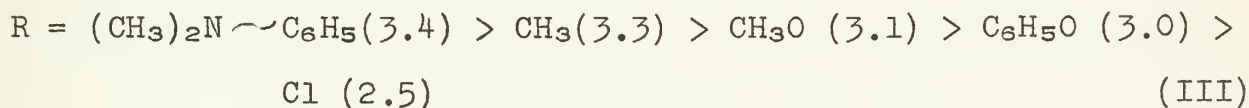
The numerous studies of nucleophilic displacement reactions on phosphorus have been reviewed and discussed by G. D. Shier (8). As these studies have been conducted in hydroxylic solvents, the possibility of large contributions from solvation of the ground and transition state make interpretation quite difficult. While a number of authors have attempted to ascertain the relative importance of bond making vs. bond breaking, solvation effects could dominate and make any statements or conclusions highly questionable.

### Recent Studies

In recent work, it has been possible to select either a non-polar solvent (tetrachloroethylene), or a non-hydroxylic solvent (1,2-dichloroethane), and in this way to minimize the effects of solvation. In the exchange of chloride-36 with  $\text{RPOCl}_2$ , reactant and product are the same chemical compound, and the formation of a symmetric transition state eliminates the effects of asymmetric charge distribution and serves to further reduce solvation effects.

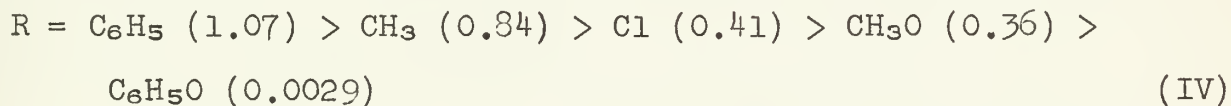
Conjugative as well as inductive effects have been found to be important in explaining the ground state properties of four-coordinate phosphorus as well as in the five-coordinate transition state. However, the relative importance of each effect changes in going from the ground state to the transition state.

Enthalpies of phenol-phosphoryl adduct formation are found to decrease in the order:



where the data in parantheses is the enthalpy in kcal/mole. Conjugative effects are shown to be of great importance and this has been confirmed by examination of the previously published NQR data (9).

By comparison, the rate of chloride-36 exchange with  $\text{RPOCl}_2$  is found to decrease in the order:



where the data in parantheses is the second order rate constant at  $-30.0^\circ$ . Here the inductive withdrawal of electron density by the groups in the trigonal plane of the five-coordinate transition state (a trigonal bipyramid) is found to be important (10).

It would be helpful if NMR studies could distinguish inductive vs. conjugative contributions; however, secondary effects have limited the interpretation of recent P-31 NMR studies. It is hoped that





further examination of phosphorus chemistry will lead to new understanding. Certainly this is a fruitful area for both organic and inorganic chemistry.

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10. Russell S. Drago, V. Alan Mode, Jack G. Kay and David L. Lydy, to be published.



## SOME APPLICATIONS OF GAS CHROMATOGRAPHY TO THE SEPARATION AND IDENTIFICATION OF METAL COMPOUNDS

James Murphy

May 25, 1965

### INTRODUCTION

Since the first applications of gas-liquid chromatography to the separation and identification of metal compounds in 1959, this technique has proven itself to be very useful and versatile. Very many volatile metal compounds are highly reactive, toxic, or explosive, and it is therefore convenient to be able to handle them in an inert atmosphere and in small quantities, which is normally the case in gas chromatography. They are often prepared by reactions which lead to a very complex mixture of products, so that an efficient technique is required to separate them. Moreover, gas chromatographic results can often be used to identify a substance, even when this substance has never been isolated before.

### DIFFICULTIES ENCOUNTERED IN THE USE OF GAS CHROMATOGRAPHY WITH METAL COMPOUNDS.

Since the vapor pressure of most metal compounds is relatively low, either high temperature or low pressure are necessary for handling the compounds in the vapor phase and for the application of gas chromatography to their separation and determination. These conditions generally decrease the efficiency of a column and severely limit the possibilities for the stationary liquid phase (1). Instruments for gas chromatography at up to 500°C are commercially available. Other instruments for work from 500°C to 1000°C have been reported (1)(2). Several liquid phases have been used in the high temperature region. These include the silicones and polyesters (1) up to 300°C and fused salt eutectics at higher temperatures (3).

The thermal stability of the compounds at high temperatures also must be considered. A restriction on the choice of materials for the instrument, solid support, and liquid phase is imposed by the reactivity of some of the compounds.

### POSSIBLE COMPOUNDS TO WHICH GAS CHROMATOGRAPHY MIGHT BE APPLIED

The following table lists the boiling points of several classes of metal compounds.

# THE HISTORY OF THE CITY OF BOSTON

The city of Boston, situated on a neck of land between the harbor and the bay, was first settled by a small number of Englishmen in 1630. The city grew rapidly, and by 1690 it had become one of the largest and most important cities in the colonies. The city was the center of the Puritan movement, and it was here that the first American Revolution began. The city was the seat of the first American government, and it was here that the first American constitution was adopted. The city was the birthplace of the American Republic, and it was here that the first American president was elected.

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# BOILING POINTS OF VARIOUS METAL COMPOUNDS

| COMPOUND                                      | BOILING POINT (°C) |
|---|--------------------|
| $\text{Sb}(\text{CH}_3)_3$                    | 80.6               |
| $\text{Bi}(\text{CH}_3)_3$                    | 110                |
| $\text{Re}(\text{CH}_3)_3$                    | 60                 |
| $\text{Fe}(\text{CO})_5$                      | 102.8              |
| $\text{Ni}(\text{CO})_4$                      | 43                 |
| $\text{W}(\text{CO})_6$                       | 175                |
| $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$ | 270                |
| $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ | 314-350            |
| $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ | 340                |
| $\text{SiH}_4$                                | -14.5              |
| $\text{B}_2\text{H}_6$                        | -92.5              |
| $\text{GeH}_4$                                | -90.0              |
| $\text{AsCl}_3$                               | 130.2              |
| $\text{GeCl}_4$                               | 83.1               |
| $\text{SiCl}_4$                               | 57.6               |
| $\text{UF}_6$                                 | 56                 |
| $\text{IrF}_6$                                | 53                 |
| $\text{MoF}_6$                                | 35                 |

The relatively low boiling points of these classes of compounds indicate the possibility of their separation and identification by gas chromatography, and this technique has been developed for use with metals, metal carbonyls, metal complexes, metal hydrides, and metal halides.

## METALS

A partial gas chromatographic separation of the constituents of a zinc-cadmium alloy was obtained on a column containing 20% LiCl on sea sand at 620°C (4).

## METAL CARBONYLS

| Compound                      | Reference |
|-------------------------------|-----------|
| $\text{W}(\text{CO})_6$       | 5         |
| $\text{Cr}(\text{CO})_6$      | 6         |
| $\pi\text{CpMn}(\text{CO})_3$ | 6         |

Hutchinson studied mixtures of metal carbonyls (5) including those of tungsten, molybdenum, and chromium, and concluded that only  $\text{W}(\text{CO})_6$  was suitable for gas chromatographic separation, but other workers (6) had previously shown that  $\text{Cr}(\text{CO})_6$  could be effectively separated and purified by gas chromatography.



ORIGINAL ARTICLES

CONTENTS

|   |   |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |     |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|

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# ORGANOMETALLIC COMPOUNDS

Many organometallic compounds have been separated, identified, and purified using gas chromatography techniques.

| Compounds   | Reference          |
|---|--------------------|
| Methyl Ferrocene  | 5                  |
| R-Hg-Br(R=CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , nC <sub>3</sub> H <sub>7</sub> , etc.)                              | 7                  |
| Si(Me) <sub>4</sub> , Ge(Me) <sub>4</sub> , Sn(Me) <sub>4</sub> , Pb(Me) <sub>4</sub>   | 8                  |
| Pb(Et) <sub>4</sub> , Ge(Et) <sub>4</sub>   | 6                  |
| Pb(Me) <sub>4</sub> , Pb(Me) <sub>3</sub> Et, Pb(Me) <sub>2</sub> Et <sub>2</sub> , Pb(Me)Et <sub>3</sub> , Pb(Et) <sub>4</sub> | 12, 13, 14         |
| SiR <sub>4</sub> and Halogen Derivatives  | 16, 17, 18, 19, 20 |
| Si <sub>2</sub> (Et) <sub>6</sub> , Ge <sub>2</sub> (Et) <sub>6</sub> , and SiGe(Et) <sub>6</sub>                               | 21                 |
| SnR <sub>4</sub> , and Halogen Derivatives  | 22, 23, 26, 9      |
| Fluoroalkyl tin   | 24, 25             |
| SnR <sub>3</sub> H, R <sub>2</sub> SnH <sub>2</sub>   | 26                 |
| Alkyl borane and diborane   | 27, 28             |
| Alkyl substituted borazoles   | 29, 30             |
| Organo arsenic  | 31, 32             |
| Organo bismuth  | 33                 |

The separation of the organometallic derivatives of the Group IVA elements has been extensively studied. Abel, et.al. (8) found that plots of molecular weight and boiling point vs. log retention time were linear for the tetramethyl derivatives of silicon, germanium, tin, and lead, and thus completely analogous to purely organic systems.

Gas chromatography has also been used as an analytical technique for the determination of tetraethyl lead in gasoline (10,11).

Pollard, et.al. (15) used gas chromatography to separate trimethyl silyl ethers and trimethyl thiosilyl ethers, to study the pyrolysis products of the methyl chlorosilanes, and rearrangement products involving the interchange of alkyl groups on silanes using AlCl<sub>3</sub> as a catalyst. The pyrolysis products of methyl chlorosilanes were also studied by Fritz and co-workers (16,17). Several quantitative determinations of alkyl silanes have also been performed (19,20)

Phillips and co-workers (29,30) have extensively studied alkyl substituted borazoles. The emphasis of the articles is on the identification of borazoles by gas chromatographic retention data.

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They have shown that once a compound has been associated with its characteristic retention time in the chromatogram, it may generally be identified again when it appears as a result of another reaction. From retention evidence, they have proposed the existence of ortho-para type isomers in the alkyl substituted borazoles.

The increased volatility of the perfluoroalkyl arsenic compounds compared with their alkyl analogs was noted by Gudzinowics, et.al. (31,32), even though a higher molecular weight group had been incorporated, ie. the retention time decreased. The same effect was noted by Sievers, et.al. in the metal complexes of acetylacetone and hexafluoroacetylacetone (34).

#### METAL COMPLEXES

The separation of metal complexes by gas chromatography has been limited to certain acetylacetonates (Acac), trifluoroacetylacetonates (TFA), and hexafluoroacetylacetonates (HFA).

| Compound Type        | Examples (M)   | Temp.      | Reference    |
|----------------------|--|------------|--------------|
| M(Acac) <sub>x</sub> | Be(II), Sc(III), Zn(II)<br>Be(II), Al(III), Cu(II)<br>V(IV), Cr(III)     | 150-200°C  | 35<br>34, 37 |
| M(TFA) <sub>x</sub>  | Be(II), Al(III), In(III),<br>Cu(II), Fe(III), Rh(III),<br>Zr(IV), Hf(IV) | 100°-150°C | 34, 37       |
| M(HFA) <sub>x</sub>  | Cr(III), Rh(III) - 30°C →  |            | 34, 37       |

Sievers et.al. (34,37,77) were able to separate the cis-trans isomers of Cr(TFA)<sub>3</sub> and Rh(TFA)<sub>3</sub>, but found it impossible to separate the d,l isomers of Cr(TFA)<sub>3</sub> using a column with 1% dibutyl-d-tartrate on glass beads, although a partial resolution had been obtained earlier (38) using gas-solid chromatography with d-quartz as the solid phase.

The possibility of using gas chromatography of complexes for quantitative analysis of metals has been suggested by several workers (37,39,41,42,77). Several new detectors have been developed (43,44,45) which extend the limits of detection to  $3.3 \times 10^{-11}$ g for Cr(HFA)<sub>3</sub> and  $4.8 \times 10^{-10}$ g for Al(HFA)<sub>3</sub> and also to increase the sensitivity for one element in the presence of another.

#### METAL HYDRIDES:

The gas chromatography techniques for metal hydrides has been extensively studied.

| Compound Type  | Reference                  |
|----------------|----------------------------|
| Silanes        | 17,46,47,48,49             |
| Germanes       | 49,50,51                   |
| Silicogermanes | 30,52                      |
| Boranes        | 53,54,55,56,57,58,59,60,61 |

The following table shows the results of the analysis of variance for the different treatments. The values are given in the order of the treatments as they appear in the table.

The results of the analysis of variance are given in the following table. The values are given in the order of the treatments as they appear in the table.

The results of the analysis of variance are given in the following table. The values are given in the order of the treatments as they appear in the table.

| Treatment | Mean | Standard Error | Sum of Squares | D.F. | Mean Square | F    | P    |
|-----------|------|----------------|----------------|------|-------------|------|------|
| Control   | 1.00 | 0.10           | 0.00           | 1    | 0.00        | 0.00 | 0.99 |
| T1        | 1.10 | 0.10           | 0.01           | 1    | 0.01        | 0.01 | 0.98 |
| T2        | 1.20 | 0.10           | 0.04           | 1    | 0.04        | 0.04 | 0.96 |
| T3        | 1.30 | 0.10           | 0.09           | 1    | 0.09        | 0.09 | 0.93 |
| T4        | 1.40 | 0.10           | 0.16           | 1    | 0.16        | 0.16 | 0.89 |
| T5        | 1.50 | 0.10           | 0.25           | 1    | 0.25        | 0.25 | 0.86 |
| T6        | 1.60 | 0.10           | 0.36           | 1    | 0.36        | 0.36 | 0.82 |
| T7        | 1.70 | 0.10           | 0.49           | 1    | 0.49        | 0.49 | 0.78 |
| T8        | 1.80 | 0.10           | 0.64           | 1    | 0.64        | 0.64 | 0.73 |
| T9        | 1.90 | 0.10           | 0.81           | 1    | 0.81        | 0.81 | 0.68 |
| T10       | 2.00 | 0.10           | 1.00           | 1    | 1.00        | 1.00 | 0.63 |

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Feher et.al. (48) have found that twenty-six silanes in one mixture could be chromatographically separated. Drake and coworkers (50,51) used gas chromatography to separate a mixture of germanium hydrides, and those higher than tetragermanes were identified solely on the basis of their chromatographic retention times. Phillips et.al. (30,52), in their studies on mixed silicon-germanium hydrides, have shown that, in certain select cases, the retention time for a compound may be predicted on the basis of retention times for the components of the compound.

A rapid quantitative determination of B-H bonds in a molecule utilizing gas chromatography has been developed (55,56). Kinetic data on the pyrolysis of diborane (57), the composition of mixtures obtained from the hydrogen reduction of  $\text{BCl}_3$  (15,8), and the identification of products from radiation induced reactions of penta and deca borane have been obtained using gas chromatography (60). A continuous preparative gas chromatograph for the purification of pentaborane (20-40g/hr) has been developed (61).

## METAL HALIDES

Gas chromatography of the metal halides is somewhat more difficult than that of the compounds previously discussed. The high boiling points and the extreme reactivity of these compounds necessitates the use of special types of apparatus for their separation.

### BOILING POINTS OF SOME METAL CHLORIDES

| Metal         | B.P. <sup>°C</sup> | Metal         | B.P. <sup>°C</sup> |
|---------------|--------------------|---------------|--------------------|
| Boron(III)    | 13                 | Niobium       | 246                |
| Silicon       | 58                 | Tantalum      | 232                |
| Germanium     | 86                 | Gold(III)     | 265 (subl.)        |
| Tin(IV)       | 114                | Molybdenum(V) | 268                |
| Arsenic(III)  | 130                | Tungsten(V)   | 275                |
| Titanium(IV)  | 136                | Mercury(II)   | 304                |
| Vanadium(V)   | 149                | Hafnium       | 317                |
| Antimony(V)   | 172                | Iron(III)     | 319                |
| Aluminum      | 178(subl.)         | Zirconium     | 331                |
| Gallium       | 215                | Tungsten(VI)  | 337                |
| Antimony(III) | 220                |               |                    |

The first part of the report deals with the general situation of the country. It is a very interesting and informative study of the country's development. The second part of the report deals with the specific details of the country's development. It is a very detailed and informative study of the country's development.

The third part of the report deals with the specific details of the country's development. It is a very detailed and informative study of the country's development. The fourth part of the report deals with the specific details of the country's development. It is a very detailed and informative study of the country's development.

The fifth part of the report deals with the specific details of the country's development. It is a very detailed and informative study of the country's development. The sixth part of the report deals with the specific details of the country's development. It is a very detailed and informative study of the country's development.

| The following table shows the results of the survey |         |       |           |
|---|---------|-------|-----------|
| Year  | Area    | Value | Unit      |
| 1950  | Area A  | 100   | Sq. Miles |
| 1951  | Area B  | 120   | Sq. Miles |
| 1952  | Area C  | 150   | Sq. Miles |
| 1953  | Area D  | 180   | Sq. Miles |
| 1954  | Area E  | 200   | Sq. Miles |
| 1955  | Area F  | 220   | Sq. Miles |
| 1956  | Area G  | 240   | Sq. Miles |
| 1957  | Area H  | 260   | Sq. Miles |
| 1958  | Area I  | 280   | Sq. Miles |
| 1959  | Area J  | 300   | Sq. Miles |
| 1960  | Area K  | 320   | Sq. Miles |
| 1961  | Area L  | 340   | Sq. Miles |
| 1962  | Area M  | 360   | Sq. Miles |
| 1963  | Area N  | 380   | Sq. Miles |
| 1964  | Area O  | 400   | Sq. Miles |
| 1965  | Area P  | 420   | Sq. Miles |
| 1966  | Area Q  | 440   | Sq. Miles |
| 1967  | Area R  | 460   | Sq. Miles |
| 1968  | Area S  | 480   | Sq. Miles |
| 1969  | Area T  | 500   | Sq. Miles |
| 1970  | Area U  | 520   | Sq. Miles |
| 1971  | Area V  | 540   | Sq. Miles |
| 1972  | Area W  | 560   | Sq. Miles |
| 1973  | Area X  | 580   | Sq. Miles |
| 1974  | Area Y  | 600   | Sq. Miles |
| 1975  | Area Z  | 620   | Sq. Miles |
| 1976  | Area AA | 640   | Sq. Miles |
| 1977  | Area AB | 660   | Sq. Miles |
| 1978  | Area AC | 680   | Sq. Miles |
| 1979  | Area AD | 700   | Sq. Miles |
| 1980  | Area AE | 720   | Sq. Miles |
| 1981  | Area AF | 740   | Sq. Miles |
| 1982  | Area AG | 760   | Sq. Miles |
| 1983  | Area AH | 780   | Sq. Miles |
| 1984  | Area AI | 800   | Sq. Miles |
| 1985  | Area AJ | 820   | Sq. Miles |
| 1986  | Area AK | 840   | Sq. Miles |
| 1987  | Area AL | 860   | Sq. Miles |
| 1988  | Area AM | 880   | Sq. Miles |
| 1989  | Area AN | 900   | Sq. Miles |
| 1990  | Area AO | 920   | Sq. Miles |
| 1991  | Area AP | 940   | Sq. Miles |
| 1992  | Area AQ | 960   | Sq. Miles |
| 1993  | Area AR | 980   | Sq. Miles |
| 1994  | Area AS | 1000  | Sq. Miles |
| 1995  | Area AT | 1020  | Sq. Miles |
| 1996  | Area AU | 1040  | Sq. Miles |
| 1997  | Area AV | 1060  | Sq. Miles |
| 1998  | Area AW | 1080  | Sq. Miles |
| 1999  | Area AX | 1100  | Sq. Miles |
| 2000  | Area AY | 1120  | Sq. Miles |
| 2001  | Area AZ | 1140  | Sq. Miles |
| 2002  | Area BA | 1160  | Sq. Miles |
| 2003  | Area BB | 1180  | Sq. Miles |
| 2004  | Area BC | 1200  | Sq. Miles |
| 2005  | Area BD | 1220  | Sq. Miles |
| 2006  | Area BE | 1240  | Sq. Miles |
| 2007  | Area BF | 1260  | Sq. Miles |
| 2008  | Area BG | 1280  | Sq. Miles |
| 2009  | Area BH | 1300  | Sq. Miles |
| 2010  | Area BI | 1320  | Sq. Miles |
| 2011  | Area BJ | 1340  | Sq. Miles |
| 2012  | Area BK | 1360  | Sq. Miles |
| 2013  | Area BL | 1380  | Sq. Miles |
| 2014  | Area BM | 1400  | Sq. Miles |
| 2015  | Area BN | 1420  | Sq. Miles |
| 2016  | Area BO | 1440  | Sq. Miles |
| 2017  | Area BP | 1460  | Sq. Miles |
| 2018  | Area BQ | 1480  | Sq. Miles |
| 2019  | Area BR | 1500  | Sq. Miles |
| 2020  | Area BS | 1520  | Sq. Miles |
| 2021  | Area BT | 1540  | Sq. Miles |
| 2022  | Area BU | 1560  | Sq. Miles |
| 2023  | Area BV | 1580  | Sq. Miles |
| 2024  | Area BW | 1600  | Sq. Miles |
| 2025  | Area BX | 1620  | Sq. Miles |
| 2026  | Area BY | 1640  | Sq. Miles |
| 2027  | Area BZ | 1660  | Sq. Miles |
| 2028  | Area CA | 1680  | Sq. Miles |
| 2029  | Area CB | 1700  | Sq. Miles |
| 2030  | Area CC | 1720  | Sq. Miles |
| 2031  | Area CD | 1740  | Sq. Miles |
| 2032  | Area CE | 1760  | Sq. Miles |
| 2033  | Area CF | 1780  | Sq. Miles |
| 2034  | Area CG | 1800  | Sq. Miles |
| 2035  | Area CH | 1820  | Sq. Miles |
| 2036  | Area CI | 1840  | Sq. Miles |
| 2037  | Area CJ | 1860  | Sq. Miles |
| 2038  | Area CK | 1880  | Sq. Miles |
| 2039  | Area CL | 1900  | Sq. Miles |
| 2040  | Area CM | 1920  | Sq. Miles |
| 2041  | Area CN | 1940  | Sq. Miles |
| 2042  | Area CO | 1960  | Sq. Miles |
| 2043  | Area CP | 1980  | Sq. Miles |
| 2044  | Area CQ | 2000  | Sq. Miles |
| 2045  | Area CR | 2020  | Sq. Miles |
| 2046  | Area CS | 2040  | Sq. Miles |
| 2047  | Area CT | 2060  | Sq. Miles |
| 2048  | Area CU | 2080  | Sq. Miles |
| 2049  | Area CV | 2100  | Sq. Miles |
| 2050  | Area CW | 2120  | Sq. Miles |
| 2051  | Area CX | 2140  | Sq. Miles |
| 2052  | Area CY | 2160  | Sq. Miles |
| 2053  | Area CZ | 2180  | Sq. Miles |
| 2054  | Area DA | 2200  | Sq. Miles |
| 2055  | Area DB | 2220  | Sq. Miles |
| 2056  | Area DC | 2240  | Sq. Miles |
| 2057  | Area DD | 2260  | Sq. Miles |
| 2058  | Area DE | 2280  | Sq. Miles |
| 2059  | Area DF | 2300  | Sq. Miles |
| 2060  | Area DG | 2320  | Sq. Miles |
| 2061  | Area DH | 2340  | Sq. Miles |
| 2062  | Area DI | 2360  | Sq. Miles |
| 2063  | Area DJ | 2380  | Sq. Miles |
| 2064  | Area DK | 2400  | Sq. Miles |
| 2065  | Area DL | 2420  | Sq. Miles |
| 2066  | Area DM | 2440  | Sq. Miles |
| 2067  | Area DN | 2460  | Sq. Miles |
| 2068  | Area DO | 2480  | Sq. Miles |
| 2069  | Area DP | 2500  | Sq. Miles |
| 2070  | Area DQ | 2520  | Sq. Miles |
| 2071  | Area DR | 2540  | Sq. Miles |
| 2072  | Area DS | 2560  | Sq. Miles |
| 2073  | Area DT | 2580  | Sq. Miles |
| 2074  | Area DU | 2600  | Sq. Miles |
| 2075  | Area DV | 2620  | Sq. Miles |
| 2076  | Area DW | 2640  | Sq. Miles |
| 2077  | Area DX | 2660  | Sq. Miles |
| 2078  | Area DY | 2680  | Sq. Miles |
| 2079  | Area DZ | 2700  | Sq. Miles |
| 2080  | Area EA | 2720  | Sq. Miles |
| 2081  | Area EB | 2740  | Sq. Miles |
| 2082  | Area EC | 2760  | Sq. Miles |
| 2083  | Area ED | 2780  | Sq. Miles |
| 2084  | Area EE | 2800  | Sq. Miles |
| 2085  | Area EF | 2820  | Sq. Miles |
| 2086  | Area EG | 2840  | Sq. Miles |
| 2087  | Area EH | 2860  | Sq. Miles |
| 2088  | Area EI | 2880  | Sq. Miles |
| 2089  | Area EJ | 2900  | Sq. Miles |
| 2090  | Area EK | 2920  | Sq. Miles |
| 2091  | Area EL | 2940  | Sq. Miles |
| 2092  | Area EM | 2960  | Sq. Miles |
| 2093  | Area EN | 2980  | Sq. Miles |
| 2094  | Area EO | 3000  | Sq. Miles |
| 2095  | Area EP | 3020  | Sq. Miles |
| 2096  | Area EQ | 3040  | Sq. Miles |
| 2097  | Area ER | 3060  | Sq. Miles |
| 2098  | Area ES | 3080  | Sq. Miles |
| 2099  | Area ET | 3100  | Sq. Miles |
| 2100  | Area EU | 3120  | Sq. Miles |
| 2101  | Area EV | 3140  | Sq. Miles |
| 2102  | Area EW | 3160  | Sq. Miles |
| 2103  | Area EX | 3180  | Sq. Miles |
| 2104  | Area EY | 3200  | Sq. Miles |
| 2105  | Area EZ | 3220  | Sq. Miles |
| 2106  | Area FA | 3240  | Sq. Miles |
| 2107  | Area FB | 3260  | Sq. Miles |
| 2108  | Area FC | 3280  | Sq. Miles |
| 2109  | Area FD | 3300  | Sq. Miles |
| 2110  | Area FE | 3320  | Sq. Miles |
| 2111  | Area FF | 3340  | Sq. Miles |
| 2112  | Area FG | 3360  | Sq. Miles |
| 2113  | Area FH | 3380  | Sq. Miles |
| 2114  | Area FI | 3400  | Sq. Miles |
| 2115  | Area FJ | 3420  | Sq. Miles |
| 2116  | Area FK | 3440  | Sq. Miles |
| 2117  | Area FL | 3460  | Sq. Miles |
| 2118  | Area FM | 3480  | Sq. Miles |
| 2119  | Area FN | 3500  | Sq. Miles |
| 2120  | Area FO | 3520  | Sq. Miles |
| 2121  | Area FP | 3540  | Sq. Miles |
| 2122  | Area FQ | 3560  | Sq. Miles |
| 2123  | Area FR | 3580  | Sq. Miles |
| 2124  | Area FS | 3600  | Sq. Miles |
| 2125  | Area FT | 3620  | Sq. Miles |
| 2126  | Area FU | 3640  | Sq. Miles |
| 2127  | Area FV | 3660  | Sq. Miles |
| 2128  | Area FW | 3680  | Sq. Miles |
| 2129  | Area FX | 3700  | Sq. Miles |
| 2130  | Area FY | 3720  | Sq. Miles |
| 2131  | Area FZ | 3740  | Sq. Miles |
| 2132  | Area GA | 3760  | Sq. Miles |
| 2133  | Area GB | 3780  | Sq. Miles |
| 2134  | Area GC | 3800  | Sq. Miles |
| 2135  | Area GD | 3820  | Sq. Miles |
| 2136  | Area GE | 3840  | Sq. Miles |
| 2137  | Area GF | 3860  | Sq. Miles |
| 2138  | Area GH | 3880  | Sq. Miles |
| 2139  | Area GI | 3900  | Sq. Miles |
| 2140  | Area GJ | 3920  | Sq. Miles |
| 2141  | Area GK | 3940  | Sq. Miles |
| 2142  | Area GL | 3960  | Sq. Miles |
| 2143  | Area GO | 3980  | Sq. Miles |
| 2144  | Area GP | 4000  | Sq. Miles |
| 2145  | Area GQ | 4020  | Sq. Miles |
| 2146  | Area GR | 4040  | Sq. Miles |
| 2147  | Area GS | 4060  | Sq. Miles |
| 2148  | Area GT | 4080  | Sq. Miles |
| 2149  | Area GU | 4100  | Sq. Miles |
| 2150  | Area GV | 4120  | Sq. Miles |
| 2151  | Area GW | 4140  | Sq. Miles |
| 2152  | Area GX | 4160  | Sq. Miles |
| 2153  | Area GY | 4180  | Sq. Miles |
| 2154  | Area GZ | 4200  | Sq. Miles |
| 2155  | Area HA | 4220  | Sq. Miles |
| 2156  | Area HB | 4240  | Sq. Miles |
| 2157  | Area HC | 4260  | Sq. Miles |
| 2158  | Area HD | 4280  | Sq. Miles |
| 2159  | Area HE | 4300  | Sq. Miles |
| 2160  | Area HF | 4320  | Sq. Miles |
| 2161  | Area HG | 4340  | Sq. Miles |
| 2162  | Area HH | 4360  | Sq. Miles |
| 2163  | Area HI | 4380  | Sq. Miles |
| 2164  | Area HJ | 4400  | Sq. Miles |
| 2165  | Area HK | 4420  | Sq. Miles |
| 2166  | Area HL | 4440  | Sq. Miles |
| 2167  | Area HM | 4460  | Sq. Miles |
| 2168  | Area HN | 4480  | Sq. Miles |
| 2169  | Area HO | 4500  | Sq. Miles |
| 2170  | Area HP | 4520  | Sq. Miles |
| 2171  | Area HQ | 4540  | Sq. Miles |
| 2172  | Area HR | 4560  | Sq. Miles |
| 2173  | Area HS | 4580  | Sq. Miles |
| 2174  | Area HT | 4600  | Sq. Miles |
| 2175  | Area HU | 4620  | Sq. Miles |
| 2176  | Area HV | 4640  | Sq. Miles |
| 2177  | Area HW | 4660  | Sq. Miles |
| 2178  | Area HX | 4680  | Sq. Miles |
| 2179  | Area HY | 4700  | Sq. Miles |
| 2180  | Area HZ | 4720  | Sq. Miles |
| 2181  | Area IA | 4740  | Sq. Miles |
| 2182  | Area IB | 4760  | Sq. Miles |
| 2183  | Area IC | 4780  | Sq. Miles |
| 2184  | Area ID | 4800  | Sq. Miles |
| 2185  | Area IE | 4820  | Sq. Miles |
| 2186  | Area IF | 4840  | Sq. Miles |
| 2187  | Area IG | 4860  | Sq. Miles |
| 2188  | Area IH | 4880  | Sq. Miles |
| 2189  | Area II | 4900  | Sq. Miles |
| 2190  | Area IJ | 4920  | Sq. Miles |
| 2191  | Area IK | 4940  | Sq. Miles |
| 2192  | Area IL | 4960  | Sq. Miles |
| 2193  | Area IO | 4980  | Sq. Miles |
| 2194  | Area IP | 5000  | Sq. Miles |
| 2195  | Area IQ | 5020  | Sq. Miles |
| 2196  | Area IR | 5040  | Sq. Miles |
| 2197  | Area IS | 5060  | Sq. Miles |
| 2198  | Area IT | 5080  | Sq. Miles |
| 2199  | Area IU | 5100  | Sq. Miles |
| 2200  | Area IV | 5120  | Sq. Miles |
| 2201  | Area IW | 5140  | Sq. Miles |
| 2202  | Area IX | 5160  | Sq. Miles |
| 2203  | Area IY | 5180  | Sq. Miles |
| 2204  | Area IZ | 5200  | Sq. Miles |
| 2205  | Area JA | 5220  | Sq. Miles |
| 2206  | Area JB | 5240  | Sq. Miles |
| 2207  | Area JC | 5260  | Sq. Miles |
| 2208  | Area JD | 5280  | Sq. Miles |
| 2209  | Area JE | 5300  | Sq. Miles |
| 2210  | Area JF | 5320  | Sq. Miles |
| 2211  | Area JG | 5340  | Sq. Miles |
| 2212  | Area JH | 5360  | Sq. Miles |
| 2213  | Area JI | 5380  | Sq. Miles |
| 2214  | Area JJ | 5400  | Sq. Miles |
| 2215  | Area JK | 5420  | Sq. Miles |
| 2216  | Area JL | 5440  | Sq. Miles |
| 2217  | Area JO | 5460  | Sq. Miles |
| 2218  | Area JP | 5480  | Sq. Miles |
| 2219  | Area JQ | 5500  | Sq. Miles |
| 2220  | Area JR | 5520  | Sq. Miles |
| 2221  | Area JS | 5540  | Sq. Miles |
| 2222  | Area JT | 5560  | Sq. Miles |
| 2223  | Area JU | 5580  | Sq. Miles |
| 2224  | Area JV | 5600  | Sq. Miles |
| 2225  | Area JW | 5620  | Sq. Miles |
| 2226  | Area JX | 5640  | Sq. Miles |
| 2227  | Area JY | 5660  | Sq. Miles |
| 2228  | Area JZ | 5680  | Sq. Miles |
| 2229  | Area KA | 5700  | Sq. Miles |
| 2230  | Area KB | 5720  | Sq. Miles |
| 2231  | Area KC | 5740  | Sq. Miles |
| 2232  | Area KD | 5760  | Sq. Miles |
| 2233  | Area KE | 5780  | Sq. Miles |
| 2234  | Area KF | 5800  | Sq. Miles |
| 2235  | Area KG | 5820  | Sq. Miles |
| 2236  | Area KH | 5840  | Sq. Miles |
| 2237  | Area KI | 5860  | Sq. Miles |
| 2238  | Area KJ | 5880  | Sq. Miles |
| 2239  | Area KK | 5900  | Sq. Miles |
| 2240  | Area KL | 5920  | Sq. Miles |
| 2241  | Area KO | 5940  | Sq. Miles |
| 2242  | Area KP | 5960  | Sq. Miles |
| 2243  | Area KQ | 5980  | Sq. Miles |
| 2244  | Area KR | 6000  | Sq. Miles |
| 2245  | Area KS | 6020  | Sq. Miles |
| 2246  | Area KT | 6040  | Sq. Miles |
| 2247  | Area KU | 6060  | Sq. Miles |
| 2248  | Area KV | 6080  | Sq. Miles |
| 2249  | Area KW | 6100  | Sq. Miles |
| 2250  | Area KX | 6120  | Sq. Miles |
| 2251  | Area KY | 6140  | Sq. Miles |
| 2252  | Area KZ | 6160  | Sq. Miles |
| 2253  | Area LA | 6180  | Sq. Miles |
| 2254  | Area LB | 6200  | Sq. Miles |
| 2255  | Area LC | 6220  | Sq. Miles |
| 2256  | Area LD | 6240  | Sq. Miles |
| 2257  | Area LE | 6260  | Sq. Miles |
| 2258  | Area LF | 6280  | Sq. Miles |
| 2259  | Area LG | 6300  | Sq. Miles |
| 2260  | Area LH | 6320  | Sq. Miles |
| 2261  | Area LI | 6340  | Sq. Miles |
| 2262  | Area LJ | 6360  | Sq. Miles |
| 2263  | Area LK | 6380  | Sq. Miles |
| 2264  | Area LL | 6400  | Sq. Miles |
| 2265  | Area LO | 6420  | Sq. Miles |
| 2266  | Area    |       |           |

GAS CHROMATOGRAPHIC SEPARATIONS OF METAL <sup>HALIDES</sup>~~HYDRIDES~~

| Compounds   | Liq. Phase  | Reference      |
|---|---|----------------|
| SnCl <sub>4</sub> , TiCl <sub>4</sub>                     | n-hexadecane                                      | 63             |
| TiCl <sub>4</sub> , NbCl <sub>5</sub> , TaCl <sub>5</sub> | n-alkanes   | 64,65          |
| AsCl <sub>3</sub> , AsCl <sub>5</sub> , SbCl <sub>3</sub> | fused   | 66             |
| SbCl <sub>5</sub> , SnCl <sub>4</sub> , TiCl <sub>4</sub> | BiCl <sub>3</sub> - PbCl <sub>2</sub><br>eutectic |                |
| UF <sub>6</sub>   | -   | 72,73,74,75,76 |

Two general types of liquid phases have been used for the separation of metal halides, organic phases (62,63,64,65) and fused salts (3,66,67). The use of organic liquids is limited in that it reacts with the metal halides (62,64,65,71), but some compounds have been separated with these liquids as partitioning agents.

Fused salt liquid phases must be chosen so that they have a low vapor pressure at the temperature of the column and so that they have a common anion with that of the solute molecules in order to minimize the possibility of undesirable reactions on the column.

Tivin (66) has shown that in some cases one may easily analyze mixtures of oxidation states, since the chlorides have different boiling points.

Tadmor has noted (69,70,71) that isotopic exchange between metal chlorides and a Cl<sup>36</sup> labeled solid phase can occur, and pure labeled compounds can be obtained in this manner. FeCl<sub>3</sub> will also undergo isotopic exchange with a Fe<sup>59</sup> labeled column containing neutron irradiated FeS as the solid phase.

#### CONCLUSION:

Gas chromatography has proven itself to be a valuable tool for the identification, purification, and separation of many types of metal compounds, but much of this field remains yet to be explored. With the development of new instruments and techniques, it should prove to be even more versatile in the future.

REPORT OF THE COMMISSIONER OF THE GENERAL LAND OFFICE

| NAME | ADDRESS | DATE |
|------|---------|------|
| ...  | ...     | ...  |
| ...  | ...     | ...  |
| ...  | ...     | ...  |
| ...  | ...     | ...  |
| ...  | ...     | ...  |

The first of the above named persons is a resident of the County of ... and the second is a resident of the County of ... The third is a resident of the County of ... and the fourth is a resident of the County of ...

The fifth is a resident of the County of ... and the sixth is a resident of the County of ... The seventh is a resident of the County of ... and the eighth is a resident of the County of ...

The ninth is a resident of the County of ... and the tenth is a resident of the County of ... The eleventh is a resident of the County of ... and the twelfth is a resident of the County of ...

The thirteenth is a resident of the County of ... and the fourteenth is a resident of the County of ... The fifteenth is a resident of the County of ... and the sixteenth is a resident of the County of ...

The seventeenth is a resident of the County of ... and the eighteenth is a resident of the County of ... The nineteenth is a resident of the County of ... and the twentieth is a resident of the County of ...

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# MEMORANDUM

TO : THE PRESIDENT

FROM : THE SECRETARY OF DEFENSE

SUBJECT: [Illegible]

[Illegible]

[Illegible]

[Illegible]

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